SUMMARY REQUIREMENTS FOR ANALYTICAL CENTER

The Analytical Center serves as the nerve center for the FFMS at the HTRW site. Operation of the perimeter air monitoring system will be continuously evaluated in the Analytical Center. Consequently, the proper design and operation of the Analytical Center is important to meeting the project's DQOs.

SECTION I: ANALYTICAL CENTER OBJECTIVES

SECTION II: ANALYTICAL CENTER SYSTEM COMPONENTS

- Structural Requirements
- Location, Utilities, Instrumentation Operation
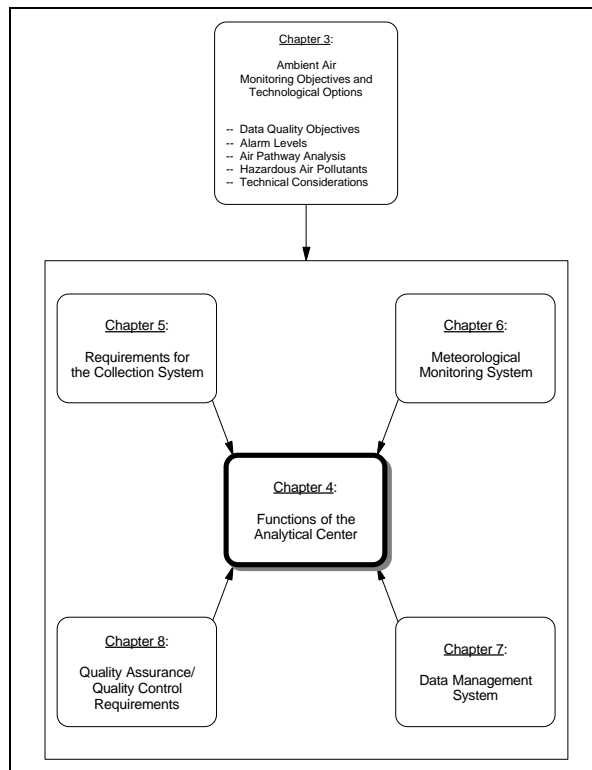
SECTION III: ANALYTICAL SYSTEMS AND OPTIONS

- NMOC Monitoring
- GC Monitoring
- GC Detectors

SECTION IV: SUPPORTING MEASURING METHODS

- EPA Compendium Methods Introduction
- Organic Compendium Methods
- Inorganic Compendium Methods

SECTION V: SYSTEM ALARM CONFIGURATION

The Analytical Center is a multiple use Center. It is therefore important that the Center be well designed, with sufficient space to allow for required operational and analytical activities, apparatus/reagents and supporting data acquisition and processing functions. This chapter addresses the various design options available in implementing an Analytical Center at a HTRW site.

Chapter 3:
Ambient Air Monitoring Objectives and Technological Options
-- Data Quality Objectives
-- Alarm Levels
-- Air Pathway Analysis
-- Hazardous Air Pollutants
-- Technical Considerations

Chapter 5:
Requirements for the Collection System

Chapter 6:
Meteorological Monitoring System

Chapter 4:
Functions of the Analytical Center

Chapter 8:
Quality Assurance/ Quality Control Requirements

Chapter 7:
Data Management System

Panel 4-1. Overview of Requirements For The Analytical Center.   **4-1**

4-1. Introduction

The Analytical Center serves as the nerve center for the real-time perimeter air monitoring program. All real-time data will be received, processed, and reported at the Center. Operation of the perimeter air monitoring system will be continuously evaluated here. Hence, most day-to-day monitoring activities will be focused in this area. The Center requires a laboratory-clean, environmentally controlled space in which to operate real-time monitoring instrumentation, collect reference method samples, perform audits, and store all electronic data and storage systems. Ideally, all power and data transmission lines should originate or route through the Center to ensure stable, continuous operation. The Analytical Center can be designed to accommodate office facilities for air monitoring personnel and house related data processing and communications equipment.

For some projects, it may be necessary for the Analytical Center to function as a self-contained, ambient-air laboratory. In addition to housing instrumentation and personnel, space is required for maintenance and equipment repair, glassware, gases, and reagents. If time-integrated air sampling is conducted during the project, the center can be designed for sample preparation, sample recovery, sample analysis, system audit and sample storage needs.

Given the multiple uses of the Center, it may be important that the Center be spacious, conveniently organized, and compartmentalized to allow for isolation of sensitive instrumentation. Design of the Center should be flexible to accommodate multiple configurations of equipment and personnel. Most importantly, design of the Center must take into account extremes in operating conditions (weather, electrical and communications load, staffing, etc.) that will no doubt be encountered during certain periods of system operations and site activities, especially for the effects of on-site, heavy equipment.

4-2. Analytical Center System Components

The Analytical Center is characterized by several functional components.

- Structural requirements.

- Location, accessibility, and security needs.

- Utility requirements.
  —Instrument/computer/communications service
  —Environmental controls

- Instrumentation, equipment and furniture needs.
  —Laboratory
  —Office
  —Sample management

• Safety facilities.

These components are described in the following sections and identified in Figure 4-1 as a suggested layout in the Analytical Center.
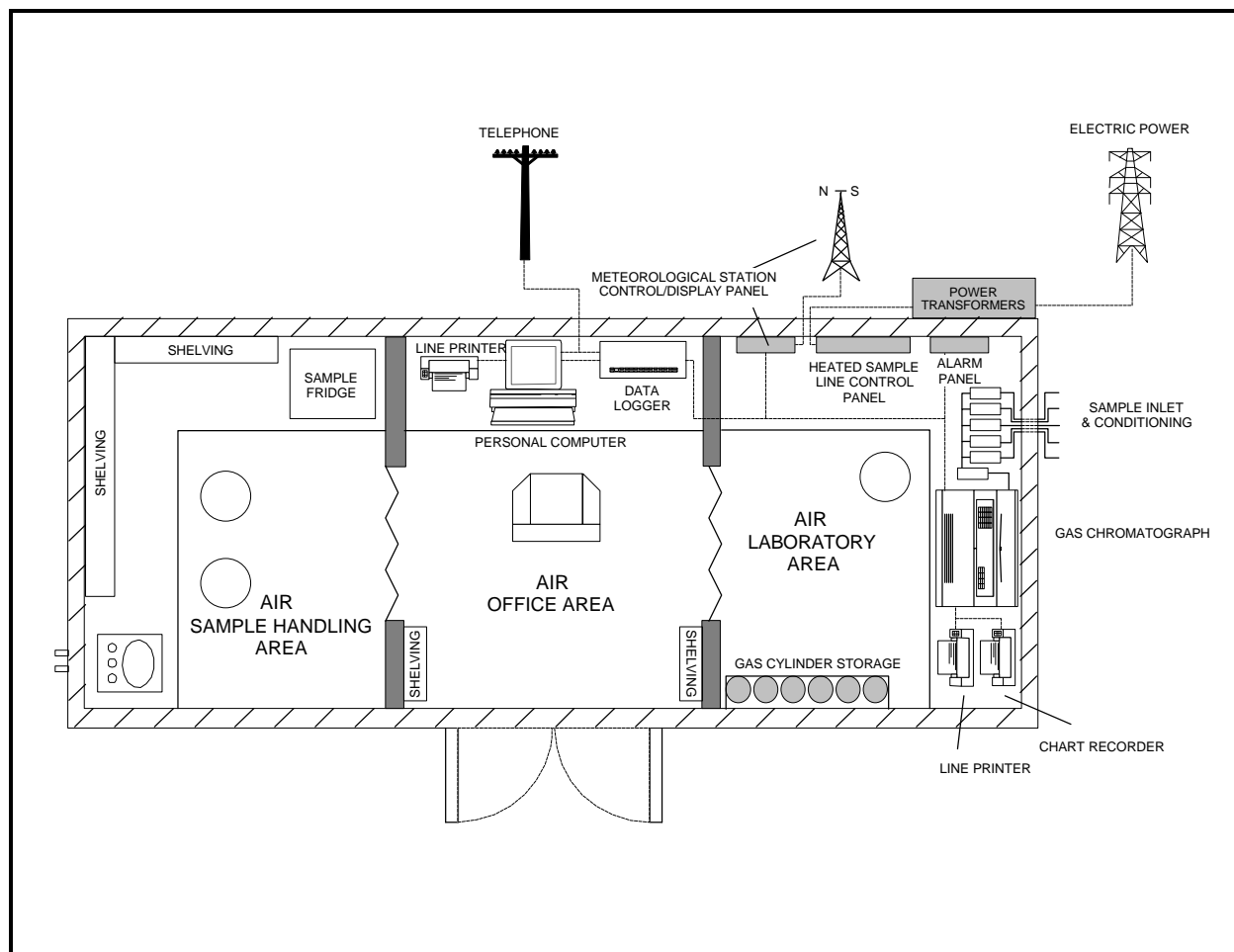

Figure 4-1. Example Analytical Center system components

a. Structural requirements. In most cases, the Analytical Center will be either a mobile or otherwise temporary structure. Many excellent prefabricated utility buildings and trailers are commercially available and can be easily modified for use. If mobile, the structure must be road safe and legal and properly weighted and balanced when fully equipped. When sited, the structure should be anchored to a solid foundation or otherwise secured to minimize vibration. The bare structure may require an area of 200 square feet or greater of space. High traffic areas, sample handling areas, and equipment storage areas should be partitioned from the analytical instrumentation to help maintain a controlled operating environment. Alternatively, it may be more

cost effective to use a second structure that requires a less stringent environment for sample handling and equipment storage.

Common building materials may be used in construction, though volatile materials such as adhesives and foam insulation should be avoided for obvious reasons. A functional window or portal should be located in each wall of the structure for entry of sample lines, wiring, communications lines, etc. The main entry and door should be no less than 36 inches wide to allow access of oversized equipment. The structure should be properly weatherized, insulated, and sealed from dust and drafts. Since cleanliness will be a constant battle, all interior surfaces such as walls, floors, and counter-tops should be smooth and easy to wipe down. Floors should be covered with heavy-weight, seamless linoleum. Tracking of dust and dirt into structures may be further minimized by attaching a small porch at the entry way. Figure 4-2 depicts an Analytical Center at a typical HTRW site.
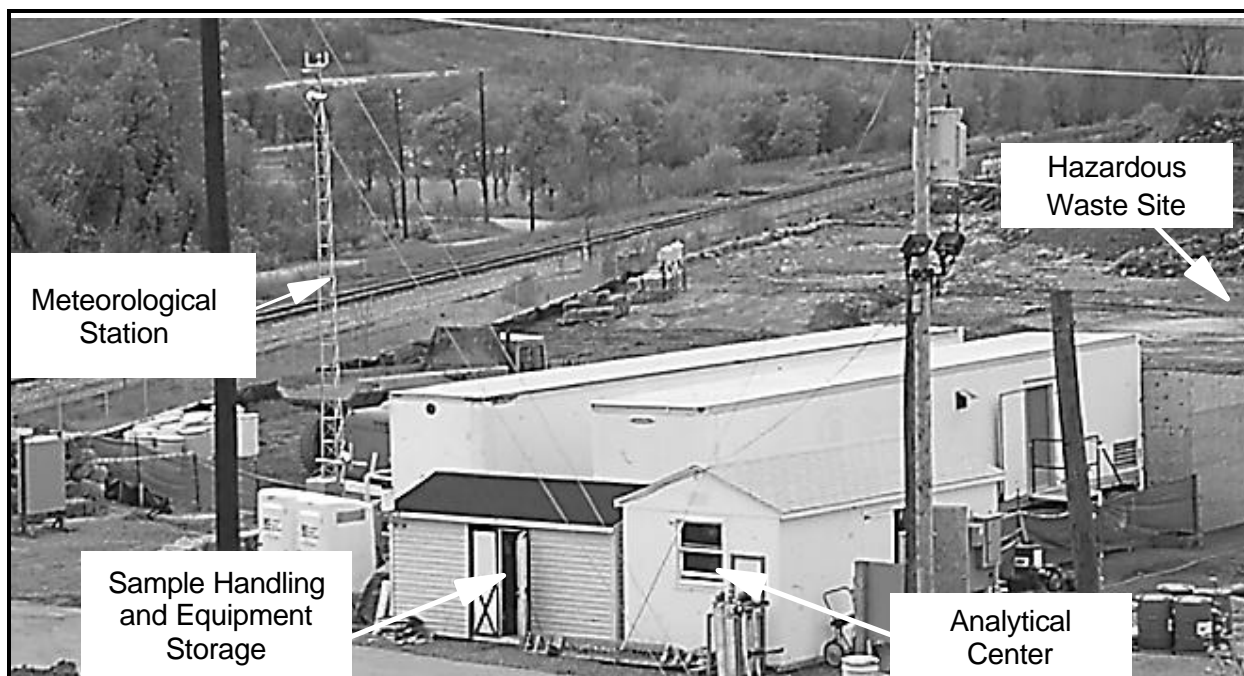

Figure 4-2. Example of a typical Analytical Center at a HTRW.

b. Location, accessibility, and security needs. The Analytical Center should be located in a convenient, easily accessible place, as close to the perimeter air sampling stations as possible. Close proximity to sampling stations will minimize the cost of and exposure to sample lines and electrical wiring. However, the advantage of proximity is offset by the need to locate the Center outside the anticipated exclusion zone and within the secure perimeter of the site. For some applications, it may be feasible to locate the analytical center on adjacent properties to minimize site activity effects.

c. Utilities. The Analytical Center will require utility services to meet the demanding specifications of the monitoring instrumentation and other equipment. These include:

- Electrical power source(s) - a variety of types of service with different amperages and phases will be necessary to accommodate multiple instrument and equipment needs under extreme operating conditions. A well-regulated constant voltage source is essential.

- Telecommunications line(s) - adequate for phone, fax, and modem to support simultaneous access to data storage system(s) and personnel.

- Gas generation/storage - adequate amount and selection of laboratory grade gases for routine instrument operation and calibration. Room temperature storage is essential.

- Water supply/wastewater disposal or storage - optional.

Configurations for these services are suggested in Figure 4-1.

Environmental conditions within the Analytical Center must be maintained to ensure maximum performance of instrumentation as well as personnel comfort. The Center should be equipped with high-capacity, electric heating, ventilation, and cooling equipment. The following are critical elements:

- Temperature - maintained at ~70 $\pm$ 5°F using electric base board heater(s)s and electric air conditioner(s) (oversized by 50 percent to compensate for equipment).

- Humidity - maintained at ~40 $\pm$ 10 percent RH using air conditioner(s).

- Dust control - maintained with high capacity electrostatic precipitator(s) or other air purifier(s).

- Lighting - incandescent or fluorescent lighting appropriate for use requirements.

- Static electricity control - use of wrist static guards during repairs of electrical components in the Analytical Center.

   d. Instrumentation, equipment, and furniture. Equipment and instrumentation employed in the Analytical Center will vary depending on the specific nature of the monitoring program. In general, the following may be items that may be essential to the Analytical Center:

- In the air laboratory (see Figure 4-3):

   —auxiliary real-time monitoring system
   —electrical control panel for heated sample line network
   —sample conditioning system including in-line particulate filters, dryers carrier gas cylinders and regulators with mounting fixtures, and auxiliary air compressor
   —microprocessor controlled sample inlet manifold
   —microprocessor controlled gas analyzer/gas chromatograph
   —calibration gas cylinders and regulators with mounting fixtures

—chart recorder
—line printer
—electrical control panel and data display for meteorological station
—electronic data logger
—audible/visible alarm system w/ telephone pager
—bench space for equipment
—cabinetry for storage of spare parts and tools

- In the air office:

—personal computer with appropriate software for data logger interface, data transfer, word processing,
  spreadsheets, and graphics
—line printer
—telephone(s)
—fax
—modem
—bench and/or desk space
—cabinetry for storage of supplies
—secure file storage
—storage for lab notebooks, equipment logs, equipment manuals, reference texts, etc.

- In the air sample management area:

—bench and/or desk space for sample handling
—cabinetry for storage of supplies
—solvent storage cabinet
—refrigerator
—dry ice storage
—sink or wash basin
—waste disposal containers
—secure storage for sample logs, Chain of Custody (COC) forms, shipping records, etc.
—storage for shipping coolers

The several partitioned spaces of the Analytical Center may be built out of or furnished with bench space, desk tops, shelving, and cabinetry appropriate for the above described uses. A suggested layout for these items is provided as Figure 4-1.
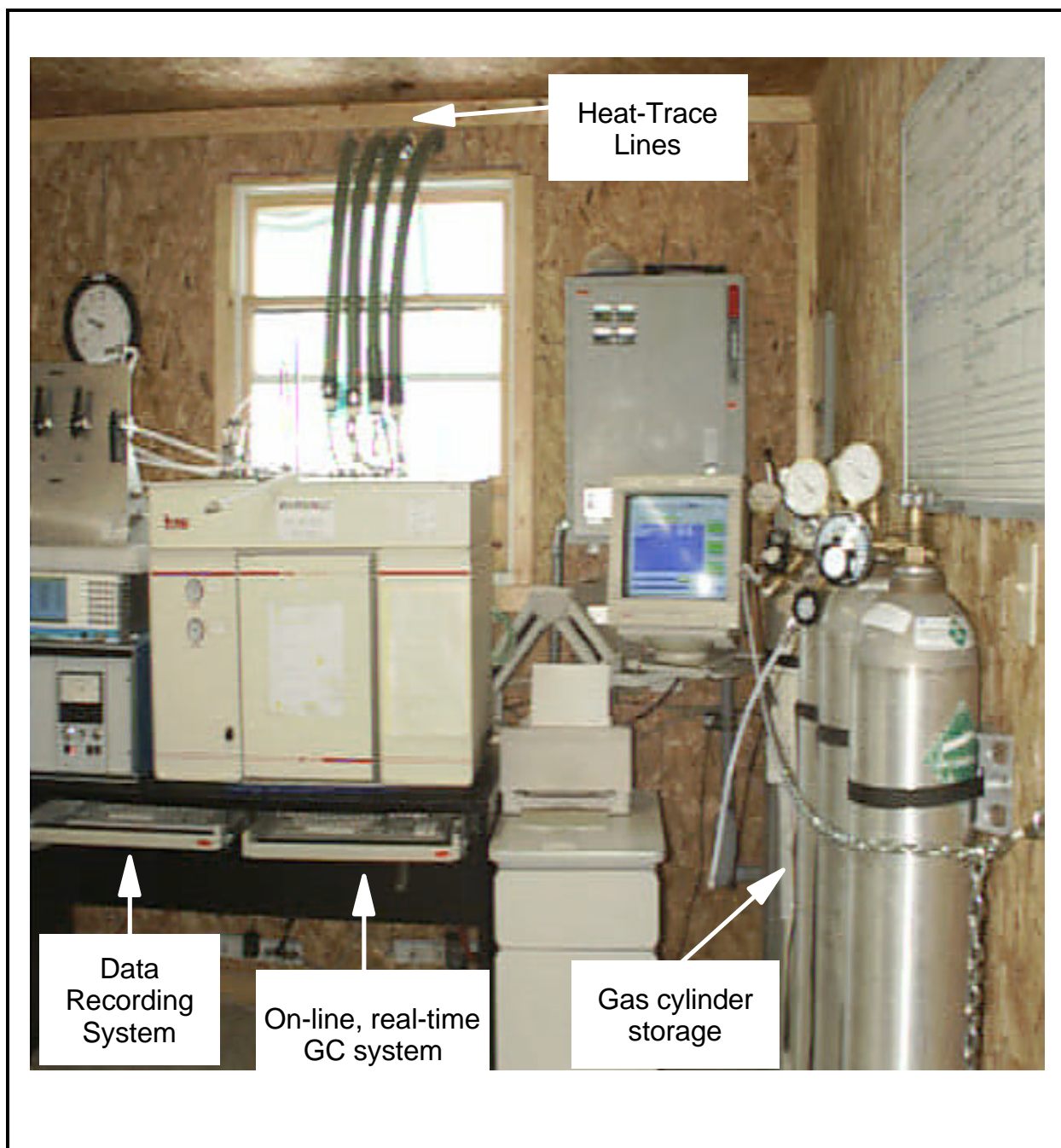
Figure 4-3. Inside of Analytical Center at a HTRW site as part of a FFMS

e. Safety facilities. The Analytical Center should be equipped with safety equipment in accordance with the Site Health and Safety Plan. At a minimum, the Center should have standard laboratory safety gear, including chemical fire extinguishers, an eye wash station, spare safety glasses, and a first aid kit. In addition, an evacuation procedure, emergency contacts, and map directions to hospital should be clearly displayed.

f. Operation and maintenance of analytical center. For many types of site activities, such as RA, the need to operate 24 hours per day has become a normal operating practice; therefore, the real-time analytical system must be able to continuously operate around the clock. This requirement means additional stress on personnel and equipment comprising the Analytical Center as part of the FFMS program. To minimize expenses and optimize productivity, several program objectives need to be identified and addressed as part of the Analytical Center SOP. Some applications may only have to coincide with site activity intervals. In such cases, the system operations may be discontinuous and require additional start-up procedures.

- For projects requiring collection of accurate and reliable data over the 24-hour period, personnel need to review monitoring data on an 8-hour schedule to minimize unacceptable data from the real-time monitoring system. Table 4-1 presents an 8-hour schedule for the Analytical Center operator in evaluation of the performance of the installed real-time monitors. Activities include observation and challenges to the analytical system.

- Other observations need to be performed associated with the support equipment in the Analytical Center to ensure continuous operation over a 24-hour period. To assist the system operator, Table 4-2 documents a typical Analytical Center checklist for continuous operations. This checklist requires the operator to observe settings associated with gas cylinders, the real-time analytical system, the meteorological system, and the data recording system

.
- Finally, for continuous operation, the Analytical Center operator needs a preventive maintenance program to follow to ensure continuous operation of the systems. In addition, guidelines need to be established to address the malfunction of various components and what corrective action needs to be initiated to bring the program back within compliance. Table 4-3 provides an example of a preventive maintenance program for continuous operation of a real-time GC system and support equipment.

- All such activities must be included in a Daily Chemical Quality Control Report (DCQCR) or equivalent record.

Table 4-1
Example Analytical Center Staffing/Schedule For Continuous Operation

Personnel	Time	Operator Onsite Time	Activities

Station Operator	Start of Continuous Operation (0700 hours)	0700-1100	• Complete Analytical Center checklist
			• Perform calibration
			  -- Internal
			  -- Single component gas
			  -- Multi-component gas
			• Verify alarm system operation

Station Operator	8-hour Shift Report (1500 hours)	1400-1600	• Complete Analytical Center checklist • Verify proper performance of 8-hr internal calibration check • Verify alarm system operation
Station Operator	8-hour Shift Report (2400 hours)	2300-0100	• Complete Analytical Center checklist • Verify proper performance of 8-hr internal calibration check • Perform single component gas calibration • Verify alarm system operation

Station Operator	8-hour Shift Report (0700 hours)	0100-0700	• Complete Analytical Center checklist
			• Verify proper performance of 8-hr internal calibration check
			• Perform calibration
			  -- Single component gas
			  -- Multi-component gas
			• Verify alarm system operation

4-3. Analytical Systems and Options

a. Non-methane organic compound monitoring. The primary motivation for conducting perimeter ambient air monitoring at a HTRW site are to (1) meet regulatory compliance requirements, (2) respond to emergency situations (chemical spills, inadvertent releases, and fires) and nuisance complaints, (3) verify to absence of off-site migration of contaminants, (4) satisfy APA requirements and data user groups, and (5) maintain system performance. Each of these areas has distinct requirements for ambient air monitoring, which are important to recognize. While each area may have distinct requirements, the impetus for monitoring programs is the risk to human health associated with exposure to the hazardous emissions. Consequently, most FFMS programs require monitoring at trigger levels to protect public health and welfare. Recent regulations have advocated an NMOC monitoring program as the first perimeter alarm level.

On April 30, 1986, the EPA promulgated Appendix E of 40 CFR 50.10, entitled *Reference Method for the Determination of Hydrocarbons Corrected for Methane.* The objective of this NAAQS was to protect the health and welfare of the individuals living in the U.S. The standard requires monitoring for NMOC using commercially available instruments that meet design and performance specifications. Specifically, any ambient

Table 4-2
Example Analytical Center Checklist For Continuous Operation

Start of Continuous Operations (0700 Hours)

I. Tank Pressures Setpoint	Tank	Outlet
G Carrier gas 60 psi	___ psi	___ psi
G Nominal 1 ppm toluene psi	___ psi	___ psi
G Nominal 1,1,1 ppm toluene, tetrachloroethane, Chlorobenzene OFF	___ psi	___ psi
G Nominal 5,5,5 ppm toluene, tetrachloroethene, Chlorobenzene OFF	___ psi	___ psi
G Nominal 10,10,10 ppm toluene, tetrachloroethene, Chlorobenzene OFF	___ psi	___ psi
G auxiliary air (compressor) 60-65 psi	NA	___ psi

II. Real-Time Gas Chromatographic System

G Initiate internal calibration with nominal 1 ppm toluene standard and compare values:

RAM Voltage	Analytical Voltage	Retention Time
_____ V (present) _____ V (previous)	_____ V (present) _____ V (previous)	_____ sec (present) _____ sec (previous) previous date/time _____
Within specs? (Y/N) _____	_____	_____

G Initiate nominal 1 ppm toluene calibration check through a selected port. Record concentration.

Gas concentration _____   Monitor response _____   % Error _____   Specification ___%
Within specs? (Y/N) _____

G   Initiate nominal 5-5-5 ppm calibration check through a selected port. Record concentrations and retention times.

	Concentration		Within spec.	Retention time (min
	Cal gas	Inst. Resp.	% Error (Y/N)	
Toluene	_____	_____	_____	_____
Tetrachloroethene	_____	_____	_____	_____
Chlorobenzene	_____	_____	_____	_____

G Carrier gas pressure   ___ (psi)   14 Set point (psi)
G Auxiliary air pressure   ___ (psi)   60-65 Set point (psi)
G Oven temperature   ___ (degrees)   70 Set point (degrees)

Table 4-2 (Continued)

II. Data System and Meteorological Monitoring

G	Wind speed	____m/s	G	NMOC (East)	____ppm
G	Wind direction	____degrees	G	NMOC (South)	____ppm
G	Barometric pressure	____mbars	G	NMOC (West)	____ppm
G	Temperature low	____degrees	G	NMOC (North)	____ppm
G	Solar radiation	____Langley			
G	Relative humidity	____%			
G	Precipitation	____% H_2O			

IV. Heat-Trace Lines

G   Line Temperatures ($°F$)

Line#1_____   Line#2_____   Specification 212$°F$ ± 25$°F$
Line#3_____   Line#4_____

V. Alarms

G   All alarms enabled.
G   External alarm enabled, tested.
G   All high threshold levels set to the perimeter action level with low levels set to 0.01 less than the high level.

VI. Printer operations

G   Verify the printer is receiving real-time data. Examine the print times for inconsistencies.
G   Ensure that the printer has sufficient paper, add as necessary.
G   Examine the print quality, replace ink cartridge as necessary.

8-Hour Shift Evaluation (1500 and 2400 Hours)

I. Tank Pressures	Tank	Outlet	Setpoint
G Carrier gas	___ psi	___ psi	60 psi
G Nominal 1 ppm toluene	___ psi	___ psi	4 psi
G Nominal 1,1,1 ppm toluene, tetrachloroethene, Chlorobenzene	___ psi	___ psi	OFF
G Nominal 5,5,5 ppm toluene, tetrachloroethene, Chlorobenzene	___ psi	___ psi	OFF
G Nominal 10,10,10 ppm toluene, tetrachloroethene, Chlorobenzene	___ psi	___ psi	OFF
G auxiliary air (compressor)	NA	___ psi	60-65 psi

Table 4-2 (Continued)

II. Gas Chromatographic System

G Record internal calibration results from the nominal 1 ppm toluene standard and compare values:

RAM Voltage	Analytical Voltage	Retention Time
_____ V (present)	_____ V (present)	_____ sec (present)
_____ V (previous)	_____ V (previous)	_____ sec (previous)
		previous date/time _____
Within specs? (Y/N) _____	_____	_____

G Initiate nominal 1 ppm toluene calibration check through a selected port. Record concentration.

Gas concentration _____   Monitor response _____   % Error _____   Specification __%__
                                                                            Within specs? (Y/N) _____

G Carrier gas pressure   ___ (psi)   14_ Set point (psi)
G Auxiliary air pressure   ___ (psi)   60-65 Set point (psi)
G Oven temperature   ___ (degrees)   70_ Set point (degrees)

III. Meteorological Monitoring

G   Wind speed   ____m/s   G   NMOC (East)   ____ppm
G   Wind direction   ____degrees   G   NMOC (South)   ____ppm
G   Barometric pressure   ____mbars   G   NMOC (West)   ____ppm
G   Temperature low   ____degrees   G   NMOC (North)   ____ppm
G   Solar radiation   ____Langley
G   Relative humidity   ____%
G   Precipitation   ____inch H_2O

IV. Heat-Trace Lines

G   Line Temperatures (°F)
          Line#1_____   Line#2_____
          Line#3_____   Line#4_____

V. Alarms

G   All alarms enabled.
G   External alarm enabled, tested.
G   All high threshold levels set to the perimeter action level with low levels set to 0.01 less than the high level.

Table 4-2 (Continued)

VI. Printer operations

G   Verify the printer is receiving real-time data. Examine the print times for inconsistencies.
G   Ensure that the printer has sufficient paper, add as necessary.
G   Examine the print quality, replace ink cartridge as necessary.

Weekly Evaluation

I. Gas Chromatographic System

Last check valve

Q	Pre-column vent flow	_____(cc/min)	_____ Set point (cc/min)
G	Detector vent flow	_____(cc/min)	_____ Set point (cc/min)
G	Sample pump vent flow	_____(cc/min)	_____ Set point (cc/min)
G	Fifth port flow	_____(L/min)	_____ Set point (L/min)

II. Heat-Trace Line

G   Weekly flow check at probe tip

	Flow (L/min)	Date last performed
Station #1	_____	_____
Station #2	_____	_____
Station #3	_____	_____
Station #4	_____	_____

G   Chemical audit at probe tip

	[TOL]	Valve	[TCE]	% Error	[CLB]			Date last performed
Station #1	_____	_____	_____	_____	_____	_____	_____	_____
Station #2	_____	_____	_____	_____	_____	_____	_____	_____
Station #3	_____	_____	_____	_____	_____	_____	_____	_____
Station #4	_____	_____	_____	_____	_____	_____	_____	_____

[TOL] = recovery of toluene in ppm
[TCE] = recovery of tetrachloroethene in ppm
[CLB] = recovery of Chlorobenzene in ppm

III. Meteorological System

G   Check battery and line voltage
    Line:_____volts   120 V setpoint
    Battery:_____volts   13 V setpoint

4-13

Table 4-2 (Continued)

Monthly Evaluation

I. Contingency Gas Chromatographic Speciated System

!	**Contingency GC Settings**		<u>Actual</u>		<u>Setpoint</u>

    G Carrier Pressure micrometer setting   _____   <u>225</u>

    G Oven Temperature   _____   <u>45</u>

    G Sample toggle switch   _____   <u>load</u>

    G Gain Setting (right end of instrument)   _____   <u>high</u>

    G Software settings. Through the channel option of the controls menu, verify the following Channel one settings:

	Temper	TEM
	Events	EVT
	Compon	CPT
	Postrun	save file and auto-inc are enabled

    G Contingency GC 3 component challenge. Initiate a 1-1-1 ppm evaluation of the GC and record the values.

Compound	Theoretical concentration	Concentration recovered	% Error	Within spec. (___%)
Toluene	_____	_____	_____	_____
Tetrachloroethene	_____	_____	_____	_____
Chlorobenzene	_____	_____	_____	_____

II. NMOC System

  G Meter reading   _____ ppm NMOC

  G Scale range   _____

  G Fine scan potentiometer setting   _____

  G Lamp light position   _____

  G Power switch   _____

  G 201 calibration. Initiate 1 ppm toluene only span check by flowing gas from a Tedlar® bag. Record value and note results:

	Gas cylinder value	_____ ppm
	201 response	_____ ppm
	percent error	_____ %
	Within ± __%	_____ (yes/no)

Table 4-3
Example of Analytical Center Preventive Maintenance Program For Continuous Operation

Parameter	Sampling method	Sampling system	Component	Symptoms	Activity
I. Volatile Organics	Real-time sample collected through sequential heat-trace sample lines and analyzed by GC/PID	Heat trace line	In-line filter	• Plugging • Low calibration gas response	• Replace with new filter • Replace with new filter
			Line temperature	• Low temperature	• Check main fuses and replace • Audit line with calibration gases • Replace line segment
			Line plugging	• No flow	• Check plugging at GC manifold • Check flow at inlet/J-Box • Replace line segment
		Gas Chromatographic System	Manifold pump	• No flow	• Check pump diaphragm • Replace with spare pump
			Sample pump	• No flow	• Check vacuum and pressure • Check pump diaphragm • Replace with spare pump
			Perma-pure dryer	• Baseline drift on chromatography	• Heat inlet and purge
			In-line filter	• No flow	• Remove, clean in alcohol, dry • Replace with spare filter
			GC column	• Poor chromatography, RT and voltage out-of-specification • Temperature	• Bake out according to maintenance procedures • Replace with spare column • Check oven flow/thermocouple • Check electronic oven board • Replace
			Detector lamp (PID)	• Poor chromatography	• Clean lamp with alcohol • Check connections and light • Replace with spare lamp
		RAM System	NMOC	• Inoperative	• Operator uses portable GC probe to record NMOC at outlet of manifold • Mobilize NMOC monitor on outlet of manifold within 4 hours

TABLE 4-3. (Continued)

	Parameter	Sampling method	Sampling system	Component	Symptoms	Activity
II.	Meteorological wind speed, wind direction, and temperature	Time-integrated through various instrument specific for meteorological parameters	Meteorological instruments	• Wind direction	• Inoperative	• Mobilize portable meteorological system within 4 hours • Contact NWS at local airport
				• Wind speed	• Inoperative	• Mobilize portable meteorological system within 4 hours • Contact NWS at local airport
				• Temperature	• Inoperative	• Check thermocouple • Mobilize portable meteorological system within 4 hours • Contact NWS at local airport
III.	Data Retrieving and Logging Systems	Real-time data retrieving and logging from real-time gas chromatographic and meteorological systems	Data logger	• System output	• Inoperative	• Follow system malfunction guidelines found in SOP • Replace with spare data logger
			Jet Printer	• System output	• Inoperative	• Follow system malfunction guidelines • Replace with strip chart recorder • Replace with spare jet printer

air monitoring can be used if it can pass the following performance specifications:

- Range (minimum) . . . . 0-5 ppm
- Minimum detectable sensitivity . . . . 0.1 ppm
- Zero/Span drift (maximum) . . . . 10%/24 hours
- Precision (minimum) 1%
- Linearity (maximum) . . . . 1% of full scale
- Operating humidity range 10-100%

While the regulation was later rescinded by EPA, commercial manufacturers made available three basic approaches for monitoring NMOC on a real-time basis. Techniques for monitoring total NMOCs are divided into three detection principles: gas chromatography, non-dispersive infrared, and ionization techniques.

In the GC technique, ambient air is extracted on a continuous basis directly into an FID where all hydrocarbons respond and produce a signal to give a total hydrocarbon (THC) content. To get an NMOC signal, an aliquot of the same air sample is introduced into a stripper column that removes water, carbon dioxide and hydrocarbons other than methane. Methane and carbon monoxide are passed quantitatively to a gas chromatographic column where they are separated. The methane is eluted first and then passed unchanged through a catalytic reduction tube into the FID. The carbon monoxide is eluted into a catalytic reduction tube, where it is reduced to methane before passing through the FID. The NMOC is calculated by subtracting the methane value from the total hydrocarbon value.

Non-dispersive infrared (NDIR) instruments operate on the principle of light absorption characteristics of certain gases. These instruments are usually subject to interferences because other gases such as water vapor and carbon dioxide may also absorb light at the same wavelength as a compound of interest. For the detection of NMOC, a particular wavelength in the infrared part of the electromagnetic spectrum is selected to represent all hydrocarbons, excluding methane. The ambient air sample enters the monitor, and organics absorb the infrared light specific for that part of the electromagnetic spectrum. A comparison is made between a reference cell containing no organics and a sample cell containing organics, which reduces the light energy reaching the detector. The difference in absorbance is directly related to concentration according to Beer's Law.

Finally, PID using UV light (instead of a flame) measures NMOC by ionizing the organics. Similar to the NDIR technique, the detector senses UV light in a particular region of the electromagnetic spectrum that represents major groups of organic compounds. This technique, however, requires the proper selection of the energy lamp used to excite the compounds. The detector senses energy given off from the excited organics and relates it to a concentration. As an example, several commercially available monitors are based upon the PID principle and are uniquely applicable to monitoring NMOC as the first level of alert around an HTRW. In operation, an ambient air sample is extracted through a multi-port valve system to a sample loop (1 mL). After several seconds, the sample loop is isolated from the gas stream, brought to atmospheric pressure, and injected past a PID, which excites the organic compounds as NMOC constituents. Because methane is not detected by the PID, the excited organics detected by the detector represents the total NMOC constituents in the sample. The monitor consequently serves as a real-time NMOC system.

The majority of the commercially available NMOC monitors are based upon the above monitoring techniques. The ambient NMOC monitors can be used as the first level of alarm for a perimeter air monitoring system at an HTRW site. Appendix E of this document identifies the manufacturers of commercially available NMOC monitors.

  b. Gas chromatography. For specific identification, GC is by far the most widely employed technique in separating HAPs in ambient air monitoring at HTRW sites. The sensitivity, specificity, and versatility of any GC system, coupled with the relatively volatile nature of most compounds make it a very attractive technique.

Basically, GC is a separation technique wherein components of a sample are separated by differential distribution between a gaseous mobile phase (usually helium, nitrogen, or hydrogen carrier gas) and a solid or liquid held on a stationary phase. In operation, the sample is injected into the carrier gas as a sharp plug, and individual components are detected as they elute from the column at characteristic "retention times" after injection. Both column temperature and carrier gas flow must be carefully controlled to obtain uniform response and retention time characteristics. The technique is similar to the widely practiced liquid-liquid partition column chromatography except that the mobile liquid phase is replaced by a moving gas phase. They are:

- Carrier gas with pressure regulator and flow meters.

- Sample injection system.

- Separation column.

- Detector.

- Data processor unit.

Gas chromatographs are highly adaptable since many variables can be involved in the selection and operation of an instrument. Column lengths, column packing materials, operating temperatures and flow rates, and sample handling equipment can all be manipulated to provide the desired results. Instruments are available with multiple columns, multiple detectors, and multiple sample handling capabilities such that several classes of compounds can be detected rapidly and simultaneously. Following is a brief discussion of the major components of a GC system.

  (1) Carrier Gas. A high pressure gas cylinder serves as the source of the carrier gas for the GC system. Commonly used gases are hydrogen, helium, and nitrogen. The carrier gas should be:

- Inert to avoid interaction with the sample or solvent.

- Able to minimize gaseous diffusion.

- Readily available and pure.

- Inexpensive.

- Suitable for detector use.

The basic function of the carrier gas is to transport the sample from the injection port through the column to the detector without interfering with the analytical technique.

(2) Injection Port. The injection port, or sample load, must be able to allow for the introduction of the sample into the system without fractionation, condensation or adsorption in other components of the system. Typically, GC systems use sample loops and are heated to insure that the integrity of the sample does not change.

(3) Chromatographic Column. Once the gas is introduced into the carrier gas stream, it is moved to the chromatographic column where separation occurs. The column is composed of a liquid phase on a solid adsorbent packed in a tube or coated on a tubular glass column.

The retention of the pollutant on the column depends upon its interaction with the solid support and liquid phase of the packing. As the carrier gas moves the pollutant through the column, the more easily adsorbed compound will be retained first while others flush through. This separation depends upon:

- Solvent properties of the support.

- Column temperature.

- Adsorbent-gas phase interaction.

- Other factors.

An important parameter to consider is response time. A column should be chosen that elutes the compounds of interest first and rather quickly. A shorter column would be preferable over a longer one to decrease response time. In commercially available monitors, column lengths vary from inches to several meters. Shorter columns do not separate compounds as efficiently or as completely as a longer column of the same material. Several short columns of different materials could be arranged to give rapid detection of several compound classes. Back flushing the columns after a designated time can be automated and prevents unwanted compounds from reaching the detectors.

Today, GC system use two different types of columns. The conventional type is called a "packed column" and consists of a solid support coated with a liquid stationary phase (gas/liquid chromatograph) or simply a solid adsorbent (gas/solid chromatography). The second type of column is a wall-coated open tubular (WCOT) or capillary column and has been widely adopted for environmental analysis packed column GC. The capillary column consists of a liquid stationary phase coated or bonded to specially treated glass or fused silica tubing. Fused silica tubing is most commonly used because of its physical durability and superior inertness. Bonded (or cross-linked) columns are used in preference to coated columns because of the greater operating temperatures that can be obtained. A significant advancement in column technology is the development of wide-bore capillary columns. These columns can be loaded at rates equivalent to packed columns, yet offer the resolution available with capillary columns.

While the use of packed columns has decreased in recent years, these columns are still very effective for many analyses. The very low boiling compounds, such as methane, chloromethane, ethylene, and others are difficult to resolve using capillary column techniques, unless cooling the compounds to subambient temperatures is possible. Packed columns using carbon molecular sieves are very effective for performing this type of analysis. Also, the stationary phase selection available on packed columns far exceeds that for capillaries.

(4) Data Handling System. The data handling system is the last component of the organic real-time monitoring system. Data handling systems can perform many tasks. Basically, the system receives the input

signal from the GC system and converts that signal to concentration. The data handling system can also provide:

- Instantaneous/averaged printout of pollutant concentration.

- Daily zero/span checks with appropriate adjustments.

- Quality control check.

- Signal warning/alert for high or out-of-control situations.

- Maintenance and input notation.

c. Gas chromatographic detectors. Once the analytes of interest have been separated by the GC system, they must be detected. The GC detection system determines, to a large extent, the specificity and sensitivity of the analysis. Consequently, one should carefully review the data quality objectives of the program when selecting a detector to be coupled with the GC system.
The primary detection types in use today are:

- FID.

- Electron Capture Detector (ECD).

- PID.

- Flame Photometric Detector (FPD).

- Mass Selective Detector (MSD).

- FTIR Detector.

- Hall Detector.

- NPD.

Table 4-4 provides an overview of the characteristics of these available detection systems. The principles of operation for many of these detectors are briefly described in this section.

(1) Flame Ionization Detector. By far the most widely used detector for a real-time, on-line FFMS is the FID. In an FID, the gas sample is introduced into a hydrogen/air flame, where the organic compounds are pyrolyzed, forming ionic intermediates. The ionic intermediates products migrate to a detector plate that is appropriately charged. The migration provides an electric current which is measured by a detector. The electronic current produced is proportional to the concentration of the species. By installing a chromatographic column preceding the detector to separate organic species, the detector can be used to detect both "total non-methane hydrocarbons" and speciated organics.

Straight chain hydrocarbons produce the greatest FID response. An FID responds differently to different compound classes. Equal amounts of hydrocarbon, esters and ethers, do not produce equal FID responses.

The sensitivity of the FID is also dependent on the relative flow rates of carrier gas, hydrogen, and air and upon electrode and linear jet geometry. However, the FID has the widest linear range of any chromatographic detector in common use, on the order of 10^{-7}, and is sensitive to as little as 10^{-11} g of alkanes. A final consideration is that the FID does not respond to water, nitrogen, nitrogen dioxide and other gases which are common to an air sample.

Several commercially available manufacturers incorporate FIDs as the detector for both total hydrocarbons and speciated organics. In addition, some of these GC systems have combined the FID and other detectors to provide greater qualitative information associated with the gas steam, as well as better sensitivity for selected groups of compounds.

Advantages of these combinations include:

- Linear response over 6 decades.

- Insensitive to air, water, and inorganic gases.

- Sensitive to most organic compounds.

- Relatively simple and inexpensive.

Disadvantages of the GC/FID combination include:

- High degree of particulate removal required.

- Semi-real-time analysis.

- Requires pure hydrogen, air and inert carrier gases.

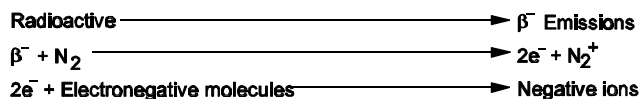- Detector susceptible to corrosion by HCl.

Particulate matter must be removed to progressively lower levels as the sensitivity of the FID is pushed higher. Particulate matter causes a noisy baseline that could overshadow a response to an organic compound. Some laboratory GC/FID instruments require 1 hour to complete the total analyses of one sample. Recent advances in high speed microparticulate packed columns has provided response times of 30 seconds where several minutes would normally be required. A continuous monitoring GC/FID has been manufactured to provide response times on the order of 1 minute; however, separation efficiency and sensitivity may decrease as the response time is decreased. Response times of less than 3 minutes would allow separation and identification of most hazardous compounds expected to be present if two or more columns were utilized.

    (2) Electron Capture Detector. The ECD technique involves exposing the gas sample to a source of electrons (usually from a Ni^{63} foil). The intensity of the electron beam arriving at a collection electrode is monitored. In essence, the ECD measures a decrease of electrical signal rather than a total electrical current. When an electron-capturing species (e.g., nitrated or halogenated organic compound) passes through the cell, the intensity of the electron beam decreases, giving rise to a signal. The carrier gas molecules are excited by a radioactive source

Table 4-4
Example of Commonly Used GC Detectors

Detector	Compounds Detected	Advantages	Limitations
Flame Ionization (FID)	Organics	Rugged and stable over extended period of time.	Not as sensitive as many other detectors. Variable response to compounds
Photoionization (PID)	Most organics except methane	Response selectivity can be varied by choice of lamp energy	Response varies from compound to compound. Less rugged than FID.
Electron Capture (ECD)	Polyhalogenated and nitro compounds	Highly sensitive and selective.	Subject to contamination. Response varies widely from compound to compound. Response drifts during temperature programming. Oxygen in air may cause analytical difficulties when direct injection is used.
Alkali Flame (NPD or AFD)	Nitrogen and phosphorus compounds	Highly sensitive and selective.	Subject to contamination. Response varies more from day to day than for FID or ECD.
Fourier Transform Infrared Spectroscopy (FTIR)	Most organics	May be highly sensitive, using long path length cells. Highly selective	Primarily a laboratory instrument. Very expensive. Water Interferences.
Flame Photometric Detector (FPD)	Sulfur or phosphorus compounds (separately)	Highly selective	Response varies from day to day. Not as sensitive as NPD for phosphorus compounds.
Hall Electrolytic Conductivity (HECD)	Halogen, sulfur, or nitrogen compounds (separately)	Highly selective. Response relatively constant from compound to compound. Stable base line during temperature programming.	Only halogen mode has been employed extensively. Requires considerable operator attention. Not as sensitive as ECD for Polyhalogenated compounds (e.g., PCB's).
Thermal Energy Analyzer (TEA)	Nitrosamines	Highly sensitive and selective.	Very expensive (~$35K).
Mass Selective Detector (MSD)	Most organics and volatile inorganics	Response is very selective and selectable for specific compounds	Very expensive (~$40K). May only detect a limited number of compounds per sample. Requires a more highly trained operator and more attention. Not usually as sensitive as FID or ECD.
Chemiluminescence Detector (CLD)	Nitrogen compounds	Highly selective and sensitive	Recently developed. Limited data on applications.

emitting Beta (to produce a steady background current under fixed applied voltage, as illustrated by the following equations:

$$\text{Radioactive} \longrightarrow \beta^- \text{ Emissions}$$
$$\beta^- + N_2 \longrightarrow 2e^- + N_2^+$$
$$2e^- + \text{Electronegative molecules} \longrightarrow \text{Negative ions}$$

The emitted high energy electrons interact with the carrier gas, which in turn interacts with the sample constituents. However, a problem can occur when the ionized sample molecules react with other sample constituents to produce an electron, which confuses the detector response. To prevent this response, a small amount of methane is added to the carrier gas (argon) to deactivate further reaction by excited molecules.

The ECD technique is highly sensitive and selective for compounds containing electron withdrawing groups, such as a halogen or nitro function group. Unfortunately, the ECD response varies widely from compound to compound, and therefore each analyte requires specific calibration to obtain quantitative data. Table 4-5 lists the relative ECD response factors for various organic compound classes. In addition, the ECD is sensitive to temperature variations, with baseline drifts of 50 percent for a temperature change in the room of only $2°C$. One must use special precautions when operating the ECD. They are:

- Ultra-pure, dry N_2 or A_r and 5 percent CH_4 to minimize contamination.

- Leak-tight gas system to reduce background noise.

- Clear gas system.

- Special precaution with operation of a Ni^{63} source.

A gas chromatograph equipped with an ECD has been successfully used in ambient air monitoring applications where sensitivities of low part per trillion for chlorofluorocarbons have been demonstrated over the long term. The Ni^{63} ECD is preferred over the tritium ECD for long-term stability and greater precision. This highly sensitive detector is suitable for trace level determination of a variety of hazardous organic species such as chlorinated aliphatic and chlorinated aromatic solvents and PCBs. In combination with an FID, a dual range instrument that is sensitive to 12 decades of concentration of organics would result. This dual detector instrument would be ideally suited to continuous monitoring applications where large swings in concentration of organics are expected. The sensitivity of the ECD requires longer restabilization times between large upsets, whereas the FID recovers more quickly.

In principle, the ECD could serve as a stand-alone detector similar to the FID and PID. However, in practice, the detector is sensitive to organic gases and other airborne components, and, hence, can only be used in a controlled gas stream (i.e., as a GC detector with a purified nitrogen or argon/methane carrier gas). In

summary, the ECD is highly sensitive, not very linear, and very sensitive to surrounding conditions, therefore probably not well suited to the rigorous demands of an on-line GC system.

Table 4-5
Electron Capture Detector Relative Response
Factors (Benzene = 1)

Factor	Compound or class
<1	Aliphatic hydrocarbons
1-10	Aromatic hydrocarbons Alcohols, ketones, ethers Monofluoro compounds
10-100	amines, esters, aldehydes, nitriles Monochloro compounds Trifluoro compounds
$100-10^3$	Dichloro aliphatic compounds (some) Stilbenes Oxalates
10^3-10^4	Dichloro aliphatic compounds (some) Monobromo compounds Hexafluoro compounds
10^4-10^6	Dichloro aromatic compounds Mononitro compounds
10^9	Monoido compounds Dibromo compounds Trichloro (or greater) compounds

Source: American Laboratory, electron Capture
            Detectors and Their Applications to Toxicology.

(3) Photoionization Detector. The PID is similar in principle to an FID and ECD except that an energy source in the UV/Visible wavelength region is used. The PID involves subjecting the gas phase compounds to a high-intensity beam of UV radiation of a particular energy. Absorption of the radiation by a gas molecule leads to formation of a positive ion and free electrons, provided the ionization potential for the compound is less than the radiation energy of the lamp, as illustrated by the following equation:

$$R + h\mu \rightarrow R^+ + e^-$$
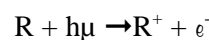
The ions are collected at an electrode, and the resultant current is monitored. The current is proportional to the analyte concentration in the gas steam.

Since the ionization potential of a particular compound must be less than the radiation energy, compounds having high ionizational potentials will be less easily detected than those of lower ionizational potential. Consequently, the choice of lamp energy will have a profound effect on the detector specificity. This aspect of PID detection is attractive from the viewpoint that using a higher energy lamp will provide a relatively nonselective, highly sensitive detector. A lower energy lamp, however, will yield a selective detector that can detect certain readily ionized compounds (e.g., aromatic hydrocarbons) but will not detect aliphatic hydrocarbons. Consequently, aromatics can be selectively detected in the presence of halogenated alkanes, using a low-energy lamp (e.g., 9.5 eV), whereas both compound classes can be detected with an 11 eV lamp. One of the most important advantages of the PID is that methane is not detected using any of the commercially available lamps and, hence, does not interfere with the analytical system when operated in the "total NMOC" mode. Table 4-6 identifies the photoionization potential of various compounds detected with various PID lamps.

The sensitivity of PID is considerably better than FID in most cases (10 ppb or better). In particular, the PID operates without combustible gases, which minimizes potential safety problems. Table 4-7 outlines different sensitivities the PID has to organic compounds relative to benzene (benzene = 1).

Several manufacturers produce GC/PID systems, which can serve as either a stand alone system or as supporting field portable system. These devices have advantages similar to the GC/FID systems in that qualitative as well as quantitative data are obtained. However, while the PID system is generally more sensitive than FID, the PID system does not give uniform responses from compound to compound. Hence, the system must be calibrated for each specific analyte to yield quantitative data.

Table 4-6
Photoionization Potential Of Several Organic Compounds

Compound	Ionization potential, eV	Compound	Ionization potential, eV
Benzene	9.25	Formaldehyde	10.87
Chlorobenzene	9.42	Vinyl chloride	9.95
o-Xylene	8.56	Ethylene oxide	10.56
m-Xylene	8.56	Acrylonitrile	10.91
p-Xylene	8.44	Allyl chloride	10.04
p-Dichlorobenzene	8.95	Chloroprene	8.80
Nitrobenzene	9.92	1,4-Dioxane	9.13
Phenol	8.50	Hexachlorocyclopentadiene	NA
o-Cresol	8.93	Methyl bromide	10.53
m-Cresol	8.98	Acetaldeyde	10.21
p-Cresol	8.97	Propylene oxide	10.22
Carbon tetrachloride	11.45	Vinylidene chloride	10.16
Chloroform	11.42	Acrolein	10.10
Methylene chloride	13.35	N-Nitrosomorpholine	NA
Methyl chloroform	11.30	Epichlorohydrin	NA
Ethylene dichloride	11.12	Maleic anhydride	9.90
Ethylene dibromide	10.44	Phosgene	11.77
Benzyl chloride	10.60	PAHs	<9
Perchloroethylene	9.32	PCBs	<8.3
Trichloroethylene	9.45	PCDDs	NA
		PCDFs	NA

NA = not applicable.

Table 4-7
Sensitivity Of Organic Compounds Relative To Benzene On A Molar Basis (Benzene = 1.0) for the PID

Sensitivity	Compound Class
<1	n-alkanes, branched/cyclic alkanes, alkenes, ketones, alkehydes, alcohols, esters
1-2	aromatic hydrocarbons, chlorobenzenes, chlorophenols, phthalates
2-3	PAHs, PCBs

A GC/PID is presently the most resistant to corrosion of the chromatographic methods. The PID is a nondestructive detector that can be purchased with Teflon®-coated internals with no decrease in sensitivity. Advantages of the PID include 10 times greater sensitivity than the FID to certain compounds, a linear range of 10^7 (10X greater than FID), and a nondestructive nature. Disadvantages include lower selectivity (inorganic compounds are also detected), drastic reductions in sensitivity due to coatings on the lamp windows, and the need for interchanging several lamps of various energies of identification of compounds. PIDs have been placed in series with FIDs as an available laboratory instrument for continuous monitoring applications. Calculating the response of the PID to that of the FID is a tool which offers further compound characterization not available with the individual detectors.

(4) Flame Photometric Detection. The FPD uses a hydrogen/air flame to decompose the compound and excite certain elements. The light emitted by certain elements (e.g., sulfur and phosphorus) is monitored by a photomultiplier tube. The element to be monitored is selected by placing an appropriate optical filter in front of the photomultiplier tube to allow only light of the particular wavelength to be detected. While several

elements could be monitored by this approach, only sulfur and phosphorus compounds (separately) are generally analyzed.

The FPD is used as a total sulfur or phosphorus detector in a stand-alone system similar to the FID for total hydrocarbons. The use of the GC/FPD is advantageous for monitoring sulfur or phosphorus-containing organics.

(5) Mass Selective Detector. A MSD determines the chemical composition of a sample by measuring the molecular weights of the molecules or molecular fragments. This determination is accomplished by converting a small quantity of a sample gas into electrically charged ions, separating the ions of differing mass-to-charge (m/e) ratios by the action of magnetic and/or electrostatic force fields, and then measuring the levels of the resulting output signals.

Mass spectrometers employ several operating components, including (1) a sample inlet system for introducing a small quantity of the substance to be analyzed into the instrument; (2) an ion source to ionize a portion of the sample; (3) a mass analyzer that separates or resolves the ions according to their mass-to-charge ratios; (4) an ion current detector that detects and amplifies the resolved ion current signals; (5) a vacuum pump to maintain a low pressure within the mass spectrometer; and (6) data processing system. These components are combined with electronics that control their functions and process the output data.

Mass spectrometers are inherently fast, sensitive, and capable of detecting wide concentration ranges because they analyze the sample in the gas phase and can detect single ions and moderate ion currents representing a wide molecular concentration range. The MS is quantitative and linear since its output is directly proportional to the concentration of the species in the sample. It is reliable and maintenance free because it is an electronically-based instrument rather than chemically based as are many single sensors. Mass spectrometers are very stable. Relative compound-to-compound sensitivities can be precisely controlled, while common-mode sensitivity variations are compensated by normalizing the outputs against measured values of known air constituents. Finally, the mass spectrometer has maximum flexibility because its broad capabilities can be selectively used under programmable microprocessor control.

A mass spectrometer identifies the chemical composition of a sample by measuring the molecular weights of its molecules or molecular fragments. The analysis (1) causes the sample to become electrically charged ions; (2) separates those ions by differing mass-to-charge ratios by magnetic/electrostatic force fields; and (3) detects those separated ions through electron multipliers.

When the mass spectrometer's magnetic field is scanned, the output appears as a series of peaks called a mass spectrum. Each peak corresponds to the ion's current intensity at a particular mass-to-charge ratio. Each chemical compound has its own unique mass spectrum (or fingerprint) caused by the statistically repeatable fragmentation of its molecules during the electron-bombardment process that creates ions. For example, Nitrogen, N_2, has a molecular weight of 28 atomic mass units (amu). When ionized under electron bombardment, it forms ions at m/e 28 from N_2^+ and at m/e 14 from N^+ (due to fragmentation) and N_2^{++} (due to double ionization). Other diatomic and triatomic molecules have correspondingly simple mass spectra and can be detected and identified based on the measurement of one or two mass peaks.

Larger molecules with more atoms have more complex mass spectra due to the greater number of different fragment ions that are formed. For example, xylene, C_8H_{10}, has a number of peaks in its mass spectrum corresponding to various ways the molecule can fragment. The information contained in the mass spectrum of xylene, in terms of the m/e values present and their intensity ratios, is sufficient to distinguish it uniquely

among all of the other compounds. The number of mass peaks required to make a compound identification depends upon the characteristics and complexity of the sample mixture.

The GC/MS techniques are particularly suited for analysis of organics using a concentration step. This technique has been used to identify organic ambient air contaminants. The concentration step involves passing the air sample through an absorber column that traps the organic material followed by thermal or solvent desorption of that material in the GC. This technique is continuous and overall response times of a GC/MS are typically greater than 3 minutes. At present, no GC/MS instrumentation is in routine use as a continuous monitor. Double mass spectrometry (MS/MS) and laser multiphoton ionization mass spectrometry have been identified as potential on-line or real-time instruments for the identification of polycyclic aromatic hydrocarbons. These instruments do not use the GC for separation of components and therefore do not involve the same delays in response time.

A disadvantage of GC/MS and MS/MS techniques is the complexity and cost of the instrumentation. Investments costing more than $75,000 are usually required. The mass spectra produced is complex and close to real time results can only be provided through a computer with extensive library searching capabilities. The MS can scan for certain compounds within seconds; however, full spectrum scans usually take greater than 3 minutes. These disadvantages should be weighed against the high sensitivity and resolution capabilities of the GC/MS system. Portable field GC/MS have become available which should be considered for FFMS application.

(6) Fourier Transform Infrared Spectroscopy (FTIR). In recent years, real-time optical monitoring has been developed which utilizes infrared detection of contaminant concentrations at HTRW sites. Obvious advantages to using optical monitoring are:

- Spectral data storage capability for identification and later evaluation.

- Semi-real-time assessment of temporal and spacial profile of HAPs from the site.

- Reasonable cost per analyte based on number of HAPs identified per sample.

- Offers both survey screening and quantitation application at HTRW sites.

Optical sensing is effective for measuring a variety of gases and volatile vapors that have absorption features in the infrared or ultra-violet spectrum.

An optical emission FTIR spectrometer can be operated in three different modes. They are:

- Closed cell mode consists of a source and detector, along with a 10-m to 30-m folded path gas cell. The sample is extracted from the ambient air and drawn into the instrument gas cell. This mode would be most applicable to HTRW, real-time detection systems providing multiple compound quantification for stable compounds.

- FTIR can also utilize an open cell mode with an external source and detector. The sample is the source emissions or ambient atmosphere along a line-of-sight between the source and detector. The current pathlength is limited to about 1,000 m but can be extended to 3 km with the addition of an auxiliary telescope. This is the most useful mode of operation for FFMS and area source emission verification.

The beam can also be aimed through test ports in incinerator stacks for source measurements as part of the remediation program.

- Emission mode is used with hot sources, such as incinerator stack plumes, where the detector is aimed at the hot vapor, which serves as its own IR source. Opaque sources, such as a smoke plume, are also readable for identification, although quantification is more difficult. Spectra show both emissions peaks due to the composition of the source itself, as well as absorption peaks from the ambient air long the path from source to detector.

The basic components of an FTIR system includes a transmitter, receiver, and electronic system. In operation, IR light projected across a cell or an open area, returned utilizing a retro reflector to the optical detection system. The heart of the optical detection system is the Michelson-type interferometer.

In this type of interferometer, a radiation is split into two paths, one going through the sample coil containing the analytical gas and the other beam going through the moving mirror, then recombined with the original path after a path difference has been introduced and an interferogram produced. Light from the sample cell can be considered to be information encoded in a light-density versus time domain. From this interferogram, a Fourier transformation is performed by computer to transform the time domain data to the wavelength domain.

Computerized data processing is also required to provide the computational power to the system to provide real-time spectra, spectrum matching, and identification and quantification of the HAPs at the HTRW site.

Interferograms of more than 300 chemicals have been identified and can be stored in the computer system as reference spectra. The established precision and accuracy is 10 percent. The accuracy of the instrument is HAPs specific. The value of 10 percent represents a reasonable upper bound for the range that is achieveable for different HAPs assuming that they are present at concentrations above the noise level. The FTIR technology is limited to IR active compounds and suffers from water interferences

(7) Dual Detectors. Combining the high sensitivity of the FID detector to easily pyrolized, low boiling organic compounds with the high sensitivity of ECD detectors to higher boiling aromatics, etc., is one method for more complete quantification of HAPs emissions from HTRW sites. One instrument could be chosen with two columns, each specified to enhance the separation of and response time associated with the appropriate organic compounds. One or both detector(s) could be used at a given time. The non destructive nature of the PID detector allows its use in series with other GC detectors. The PID/FID, PID/ECD and PID/NPD combinations have all been used for specific applications. A typical PID/FID application is the identification of hydrocarbon classes. The PID response increases with increasing degrees of unsaturation and the FID response is mostly unaffected by double bonds. In comparison, the reactive response of these two detectors, alkanes, olefins, and aromatic compound classes can be identified in complex sample matrices.

In summary, the selection of the appropriate detector depends upon the analyte of concern, the level at which it must be detected, and the responsiveness of the system to the environment in which the analyte is a part. Table 4-8 summarizes the characteristics of the various detectors in combination with GC systems, while Figure 4-4 compares detection limits of the detectors discussed. Table 4-9 identifies useful detector combinations in HAPs monitoring and detection, while Table 4-10 provides guidelines, advantages, and limitations associated with useful GC detector combinations.

d. Combination NMOC/speciated gas chromatographic system. In recent years, regulatory agencies responsible for monitoring emissions from HTRW sites have required the monitoring of both NMOC and

speciated organic compounds as part of the FFMS program to meet the data quality objectives of the remediation air program. An example approach could require that an NMOC trigger level be established at the perimeter of the HTRW site to which additional speciated organic monitoring is to occur if the trigger level is exceeded. The perimeter monitoring would include:

- NMOC perimeter trigger level. As an example, an average NMOC concentration level of greater than 1 ppm would trigger organic speciation compound identification by the analytical system, as illustrated in Figure 4-5.

- Speciated compound identification. If the NMOC is determined to be greater than 1 ppm, the analytical system immediately speciates the air sample to determine if the agreed upon PALs has been exceeded, as illustrated in Figure 4-6.

- Net concentration. If the PAL is exceeded, the data system that determines the net concentration by subtracting the upwind station concentration for that analyte from the downwind station concentration to determine the influence of HTRW site on the community, as illustrated in Figure 4-7.

HTRW projects may require the monitoring of NMOC and speciated VOCs by incorporating monitoring system using sample transport lines to collect samples from different locations around the perimeter of the HTRW site.

Real-time perimeter air monitoring system for evaluating NMOC and speciated organics by GC equipped with two photoionization detectors could be constructed or purchased to analyze multi-sampling probes extending to various points on the site perimeter. Such a system could provide both an automated NMOC mode and a speciated VOC mode. The system provides for automatic and real-time monitoring of NMOC and speciated VOCs in the low ppb to percent range.

This example system involves a photoionization detector in the analytical center with a microprocessor control, which allows it to operate in the "real-time mode." The unit rapidly scans several sampling points around the perimeter of the HTRW site in the "Rapid Analytical Mode (RAM)" for NMOC, without methane interference, and then automatically switches to a chromatographic mode when the "RAM" mode indicates the presence of unacceptable levels of NMOC, as illustrated in Figure 4-8.

The basic components of the analytical system include:

- Multipoint sequencer.

- "RAM" NMOC concentration mode.

- Analytical GC speciated VOC mode.

- Dual NMOC/VOC alarm levels.

- Data processing of NMOC/speciated VOC concentrations.

Multiple heat-trace sample lines extract ambient air from around the HTRW site and transports the air sample to the real-time, on-line GC system with multipoint sequencer located in the Analytical Center.

The multipoint sequencer consists of numerous solenoid valves controlled by the microprocessor so that one sample at a time is switched to the sampling manifold while all others are vented to the exhaust pump. This design allows the sample to flow continuously through the heated sampling lines; therefore, a fresh sample is always available for analysis. The valve compartment contains separate handling and autocalibration components together with the manifold sampling pump, carrier gas controls, and a 10-port sampling valve.

Table 4-8
Example Characteristics Of Various Common Detectors Used as Part of FFMSs at HTRW Sites

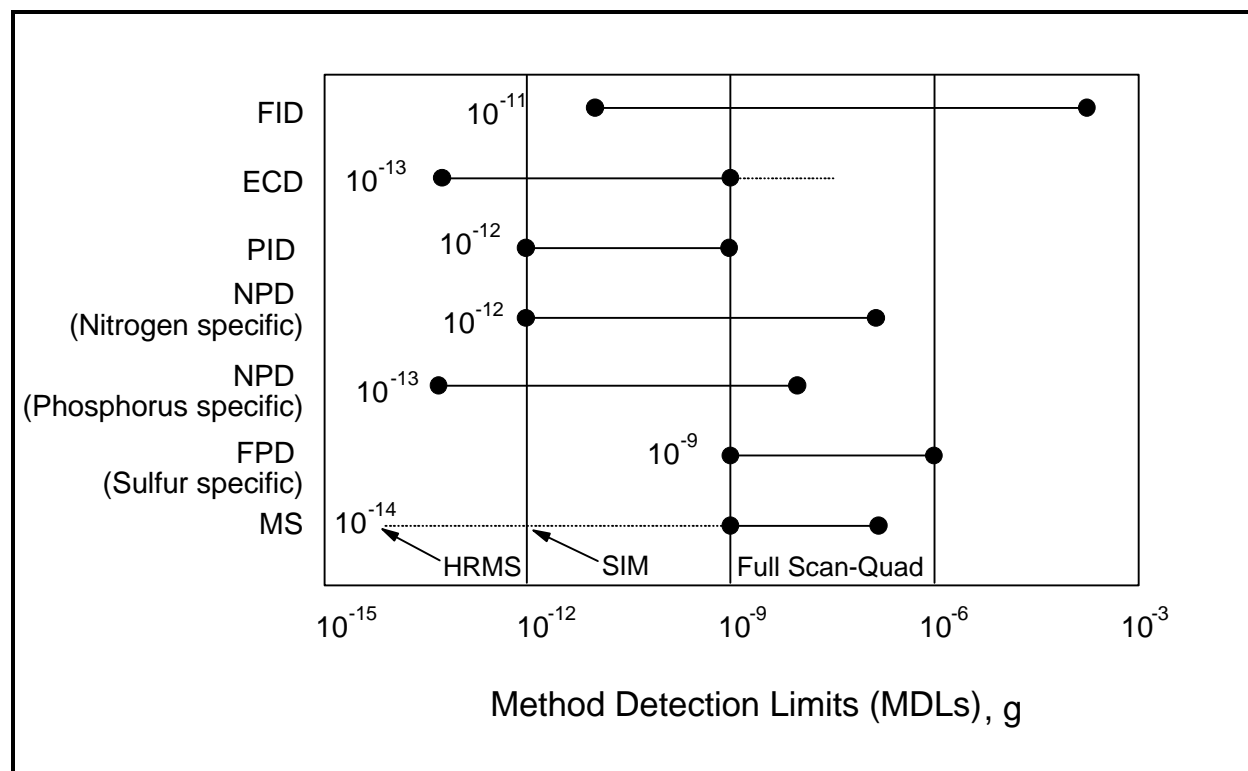| Category	Detector		
	ECD	FID	PID
Minimum quantity	10^{-14} g/sec	10^{-11} to 10^{-12} g/sec (~0.50 ppb)	10^{-12} g
Response	Extremely selective electronegative compounds	Selective only organics	Selective response (change UV source)
Linearity	1 to 10^5	1 to 10^5	1 to 10^6
Stability	Fair	Excellent	Fair
Carrier gas	He or H_2	Nitrogen/Helium	Nitrogen/Helium
Temperature limit	325°C	400°C	300°C

Figure 4-4. GC detector comparison associated with method detection limits

Table 4-9
Examples of Useful GC Detector Combinations

Detector Combination	Application
ECD-PID (Series)	Volatile aromatics and chlorinated solvents
PID-FID (Series)	Aromatic hydrocarbons
ECD-FID (Series)	Chlorinated hydrocarbons
NPD-FID (Parallel)	Nitrogen or phosphorous compounds
FPD-FID (Parallel)	Sulfur compounds
PID-NPD (Series)	Amines
MS-FID (Parallel)	Aromatic and halogenated volatile compounds
ECD-FID (Parallel)	Aromatic and halogenated volatile compounds
ECD-PID-FID (Parallel)	Aromatic and halogenated volatile compounds

Table 4-10
Example of Common GC Detectors, Detection Limits, And Advantages/limitations

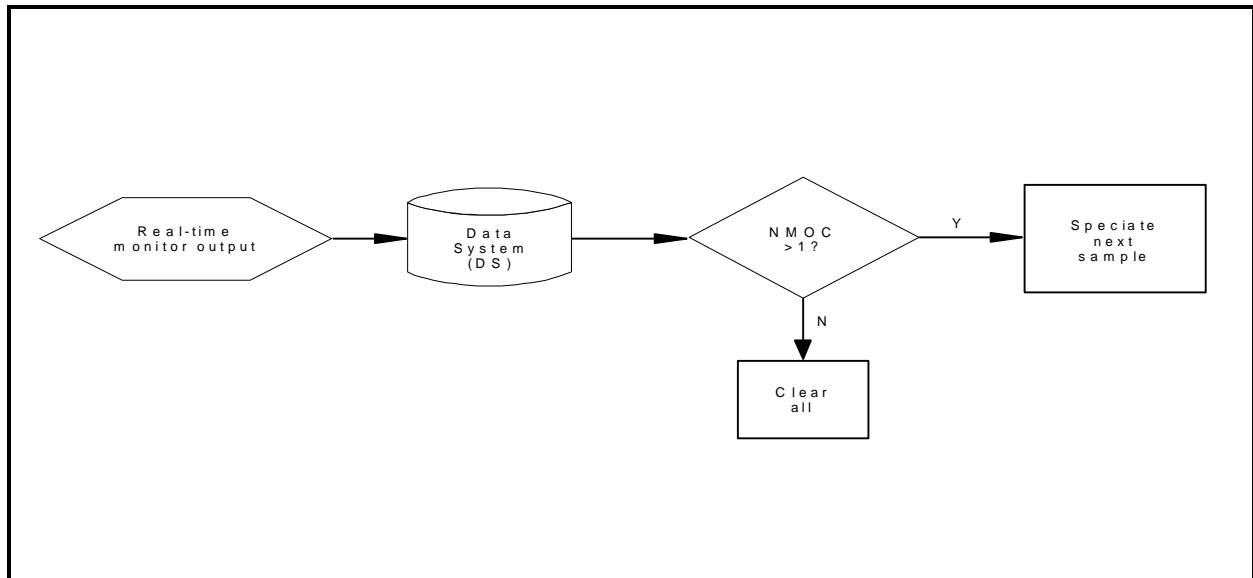| Detector	Compounds Detected	Advantages	Limitations	Detection Limits (ng/m^3)
Flame Ionization (FID)	Non-halogenated organics; PAHs	Response is relative constant from one compound to another	Not as sensitive as many of the other detectors	5-100
Photoionization (PID)	Most organics except methane; aromatic organics	Response selectively can be varied by choice of lamp energy	Response varies from compound to compound. Less rugged than FID	25-100
Electron Capture (ECD)	Polyhalogenated and nitrogenated organics	Highly sensitive and selective Response drifts during temperature programming	Subject to contamination. Response varies widely from compound to compound.	5-100
Flame photometric Detector (FPD)	Sulfur or phosphorus compounds (separately)	Highly selective	Response varies from day to day. Not as sensitive as NPD for phosphorus compounds	5-500

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│                                                                               │
│   ⬡ Real-time    →  [Data        ]  →  ◇ NMOC  ◇  ──Y──→  [Speciate  ]        │
│     monitor output    System (DS)        > 1 ?              next sample       │
│                                            │                                   │
│                                            N                                   │
│                                            ↓                                   │
│                                          [Clear all]                          │
│                                                                               │
└─────────────────────────────────────────────────────────────────────────────┘
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Figure 4-5. Example of schematic for NMOC decision mode.

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┌─────────────────────────────────────────────────────────────────────────────┐
│                     ⬡ Real-time                                               │
│                       monitor output                                          │
│                            ↓                                                   │
│                       [Data System (DS)]                                      │
│                            ↓                                                   │
│           ◇ Is NMOC ◇ ──Y──→ ◇ Is this an ◇ ──N──→ [Speciate ] → [If station │
│             >1 ppm            upwind station?         sample ]     is >PAL,    │
│               │                   │                               initiate    │
│               N                   Y                               speciation  │
│               ↓                   ↓                               of upwind   │
│           [Clear all]         [No further                         sample ]    │
│                                action ]                                        │
└─────────────────────────────────────────────────────────────────────────────┘
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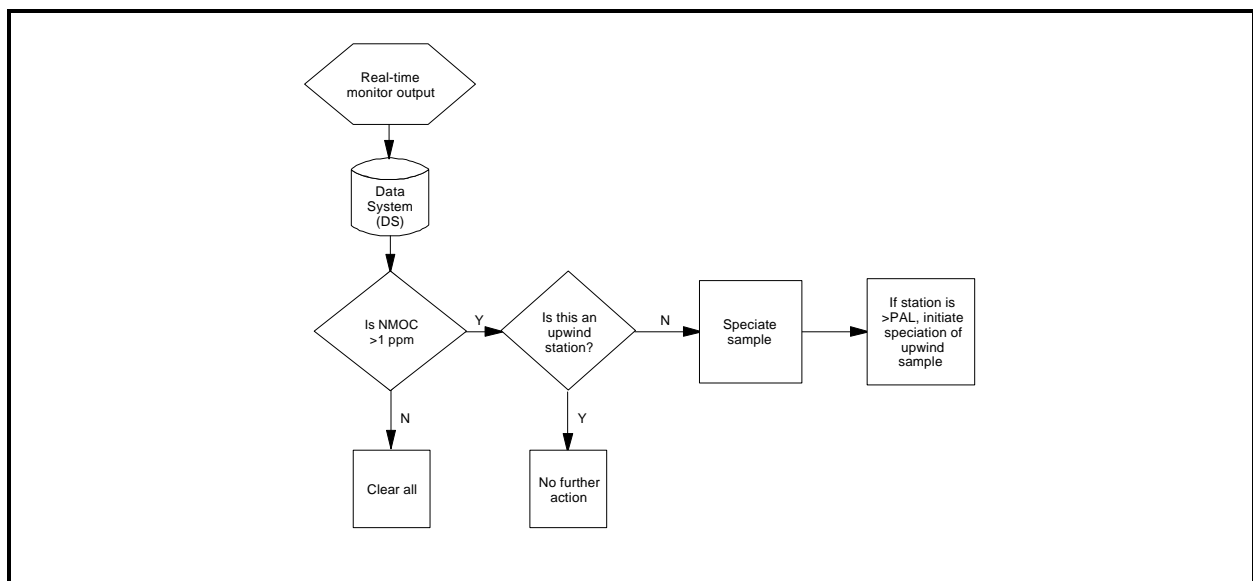
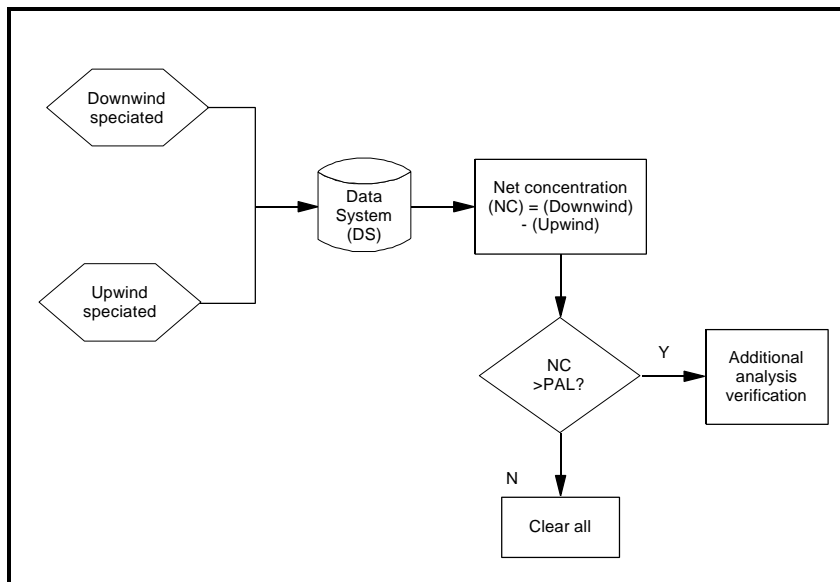**Figure 4-6. Example of schematic for speciated decision mode**

Figure 4-7. Schematic of net concentration decision mode

In operation, ambient air is pulled, from sample inlet locations into the inlet of the sample transfer lines at each of the HTRW perimeter locations, passed through an in-line heated filter to remove particles, then passed on through to the real-time, on-line GC system in the Analytical Center. The multi-point sequencer rotates in the GC system manifold from each of the perimeter sampling points. The process is controlled by a micro-processor, allowing one ambient air sample at a time to be switched to the sample loop while all others are vented, thus providing a "fresh" sample to the analyzer during a sample event. The ambient air sample enters the system to a sample loop, as illustrated in Figure 4-9. After a predetermined period, the sample loop is isolated from the sample gas stream, purged with nitrogen gas where the VOCs are directed to the first PID, by-passing the GC column. In this "RAM" mode, the column is bypassed and the sample is directed to the first PID. The "RAM" mode provides total NMOC concentration in the gas stream. The whole system is under microprocessor control and the switch from "RAM" to chromatographic speciated analysis is initiated when the "RAM" average NMOC measurement exceeds 1 ppm. When the NMOC average value is >1 ppm, a speciated analysis is performed on the extracted ambient air sample. In the "analytical mode," the analyzer performs a gas chromatographic separation of VOC components in the sample. As the nitrogen gas stream containing the extracted VOCs passes through the capillary GC column, the contaminants interact with the inner coated walls on the capillary column, thus enabling separation. As the individual contaminants exit the GC column, their presence are detected by a second PID. The response of the detector is directly proportional to the concentration of analyte in the nitrogen gas stream. Analytical identification is determined by performing multipoint calibration of the system, using retention time as the identification technique. Due to detection limitations and number of target compounds, real-time on-line monitoring allows only for a definitive list of VOCs (up to 15 compounds) to be monitored at any one sample point..

e. Manufacturers of monitoring systems. This section discusses the various aspects of monitoring systems applicable to HTRW sites for characterizing NMOC and speciated organics emissions. Appendix F provides a listing of numerous manufacturers of these systems as a system design starting point.
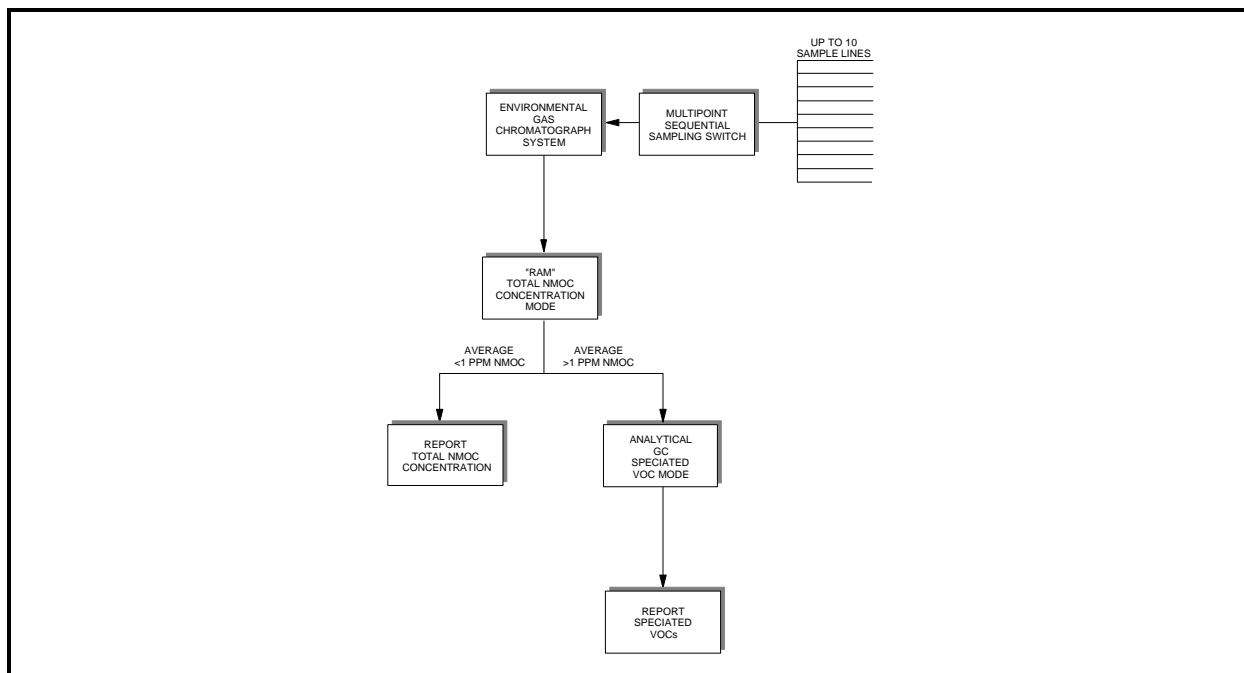
Figure 4-8. Schematic of real-time gas chromatograph system with NMOC "RAM" and speciation VOC modes (functions)

4-4. Supporting Measuring Methods

a. Introduction. As specified in CERCLA and SARA regulations, the EPA has the responsibility for assessing and characterizing all contaminant migration pathways from waste to the environment and the resulting environmental impacts. Specifically, the regulations specify that "all potential migration pathways for contaminants" be characterized and quantified. In addition, all emissions from HTRW site during remediation must be within compliance with Federal and State ARAR and other nonbinding criteria "to-be-considered (TBC)" emission limits. These requirements include not only local, State, or community standards, but also the NAAQS. Over the last 25 years, EPA has developed national standards for seven criteria pollutants. The seven primary criteria pollutants are SO_2, NO_x, O_3, CO, TSP matter as PM_{10}, Pb, and NO_2. The NMOC was promulgated, then rescinded (however, the NMOC is still used). Table 4-11 identifies the criteria pollutants, the averaging time for those pollutants, the associated standards for each of the pollutants, and the Reference Measurement Method (RMM) to be used to quantitate them. Monitoring at HTRW sites may require the application of EPA's RMMs to demonstrate compliance or to be operated collocated with the real-time on-line FFMS. In ambient air monitoring for criteria pollutants, there are two sampling and analytical designated methodologies:
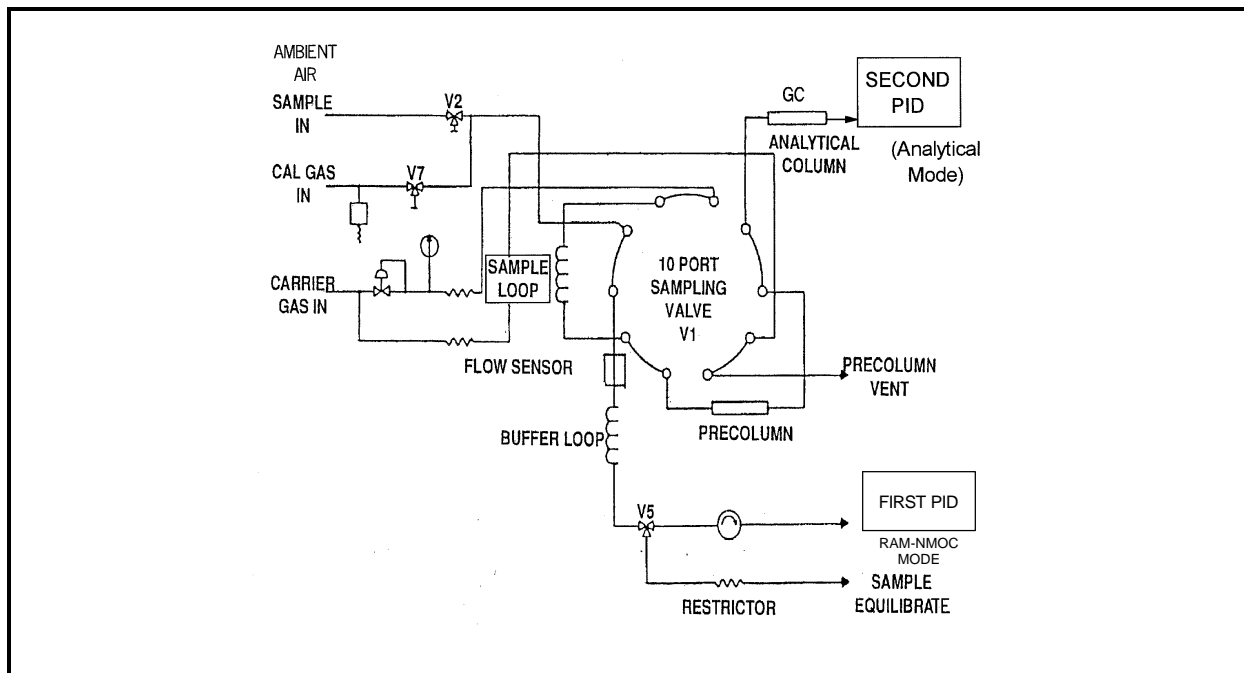
Figure 4-9. Example of a commercially available multi-port NMOC/analytical gas chromatographic system for HTRW applications

- Reference Measurement Method. One specific method of analysis for a particular pollutant that has been promulgated by EPA for criteria pollutant measurement.

- Equivalent or Reference Method. A method that has been found experimentally accurate enough by EPA to match analysis specifications given for the reference methods (range, precision, and sensitivity) or have been made available through EPA guidance documents. In terms of methods which can be used to support a FFMS, either promulgated or guidance methods can be reference methods. These methods can also be used as contingency or off-site methods.

These methods (reference and equivalent) were chosen by the EPA after a comprehensive review of available methodologies for measuring the criteria pollutants. Although, perhaps not representative of "state-of-the-art" techniques, these methods have been carefully evaluated and errors and/or interferences quantified where possible. They also represent the methods required or accepted by EPA for use at most HTRW remedial active sites. In most situations, air methods that have been made available as guidance methods are accepted as a reference method for some HTRW applications.

Table 4-11
Criteria Pollutants and Their Reference Methods

Pollutant	Averaging time	Primary standards[b,c]	Secondary standards[d]	Reference measurement method[e]
Sulfur dioxide (SO_2)	Annual arithmetic mean	80 µg/m^3 (O.03 ppm)		Pararosaniline method
	24 hr	365 µg/m^3 (0.14 ppm)		
	3 hr	--	1,300 µg/m^3	
Suspended particulate matter (SPM) As PM_{10}	Annual geometric mean	50 µg/m^3		High volume sampling method
	24 hr	150 µg/m^3		
Carbon monoxide (CO)	8 hr	10 mg/m^3 (9 ppm)	Same as primary standard	Nondispersive infrared spectroscopy
	1 hr	40 µg/m^3 (35 ppm)		
Ozone (O_3)	1 hr	0.12 ppm	Same as primary standard	Gas-phase chemiluminescent method with ethylene
Hydrocarbons (corrected for methane) [rescinded]	3 hr (6 to 9 a.m.)	160 µg/m^3 (0.24 ppm)	Same as primary standard	Flame ionization detection using gas chromatography
Nitrogen dioxide (NO_2)	Annual arithmetic mean	100 µg/m^3 (0.05 ppm)	Same as primary standard	Gas-phase chemiluminescence with ozone
	1 hr	0.25 ppm		
Lead (Pb)	Calendar quarter	1.5 µg/m^3	Same as primary standard	High volume sampling, atomic absorption analysis

a Environmental Protection Agency, *Federal Register* 40 CFR 50 p. 4-6 (July 1, 1979).
b National standards other than those based on annual arithmetic means, annual geometric means, or quarterly arithmetic means are not to be exceeded more than once per year.
c National Primary Standards: The levels of air quality necessary, with an adequate margin of safety, to protect the public health.
d National Secondary Standards: The levels of air quality necessary to protect the public welfare from any known or anticipated adverse effects of a pollutant.
e Reference method as described by EPA. An "equivalent method" means any method of sampling and analysis which can be determined to have a "consistent relationship to the reference method."

An RMM may be either manual or automated. If manual, it is a detailed chemical procedure specifying all important parameters. If automated, it consists of a measurement principle (MP) and a calibration principle (CP). Thus for an automated method, any instrument using the measurement principle (designated by the EPA) is a separate reference method. Among the gases, SO_2 is the only manual Reference Method. Nitrogen dioxide, O_3, CO, and hydrocarbon (HC) use automated methods and thus follow a particular measurement principle; there are several reference methods for each.

The Federal Reference Methods (i.e., the complete description of the procedure for manual methods and the detailing of the MP and CP for automated Method) are contained in the Appendices to 40 CFR 50.

   b. EPA compendium methods. Historically, VOCs are not addressed as criteria pollutants, and thus do not have associated reference or equivalent sampling and analytical methodology. The monitoring and analytical techniques of VOCs were based on professional judgments rather than adherence to any documented uniform guidelines. As a result, there was little consistency among the sampling and analysis procedures and the intended uses of the data. The absence of standardized procedures left many deficiencies in air monitoring programs and raised serious concerns about the comparability of the data.

The EPA has developed two ambient air compendia to address these deficiencies. They are:

   • *Compendium of Methods for Determination of Toxic Organic Compounds in Ambient Air.*

   • *Compendium of Methods for the Determination of Inorganic Compounds in Ambient Air.*

The Compendia have been prepared to provide Regional, State, and local environmental regulatory agencies, as well as other interested parties, with methods that can be used as RRMs. These guidance methods are generally used for determination of selected HAPs at HTRW sites. The Organic Compendium contains 17 methods, as illustrated in Figure 4-10 while the Inorganic Compendium contains five methods, as illustrated in Figure 4-11.

While the Compendium methods are guidance methods they are frequently utilized as RMM for HTRW projects   The majority of the methods address monitoring for classes of compounds, i.e., volatile and semi-volatile organics, inorganic compounds, while other methods address specific HAPs. Table 4-12 outlines a brief description and applicability for each of the Organic and Inorganic Compendium methods.

   (1) *EPA Organic Compendium*.

   (a) *Organic Compendium Method TO-1: Volatile Organic Compounds (80° to 200°C)*. Volatile organic compounds are emitted into the atmosphere from a variety of activities at an HTRW site. Many of these compounds are toxic; hence knowledge of the levels of such materials in the ambient atmosphere is required to determine human health impacts. Conventional air monitoring methods (e.g., for workspace monitoring) have relied on carbon adsorption approaches with subsequent solvent desorption. Such techniques allow subsequent injection of only a small portion, typically 1 to 5 percent of the sample onto the GC system. However, typical ambient air concentrations of these compounds require a more sensitive approach. The thermal desorption process, wherein the entire sample is introduced into the analytical (GC/MS) system, fulfills this need for enhanced sensitivity.

Organic Compendium Method TO-1, which may be replaced with TO-17, describes a generalized protocol for the collection and determination of certain VOCs that can be captured on Tenax® GC [poly(2,6-diphenyl phenylene oxide)] and determined by thermal desorption GC/MS techniques, as illustrated in Figure 4-12. The method is applicable to nonpolar organics having boiling points in the range of approximately 80° to 200°C.

Sampling involves drawing ambient air through a cartridge containing ~1 to 2 grams of Tenax®. Certain VOCs are trapped on the resin while highly volatile organic compounds and most inorganic atmospheric constituents
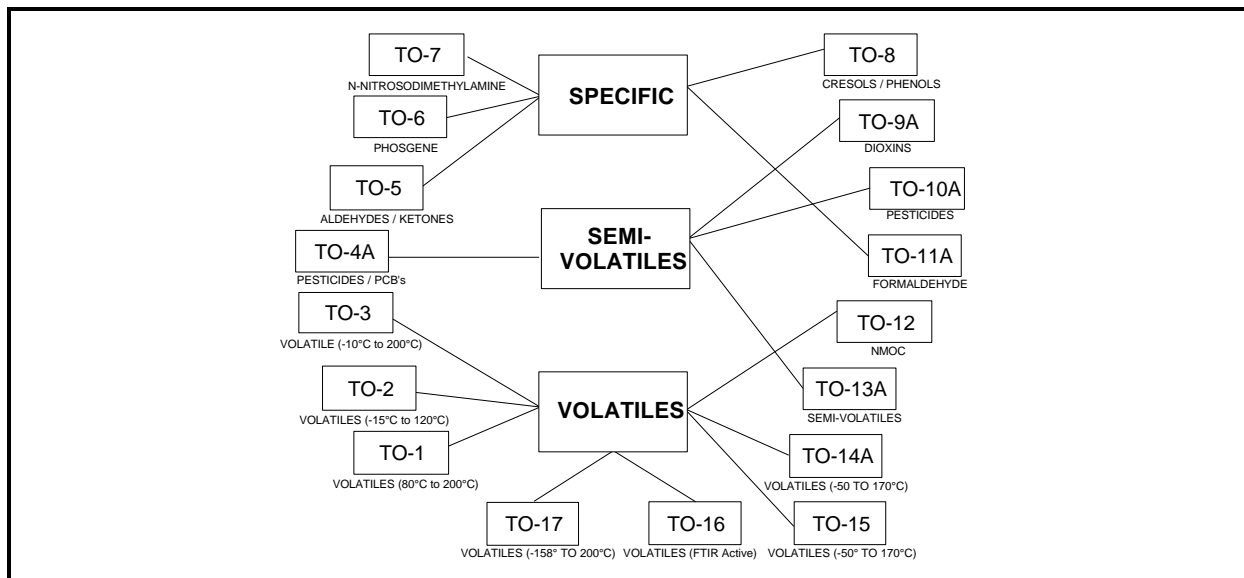
Figure 4-10. Compendium of organic methods for sampling and analysis of HAPs at HTRW sites
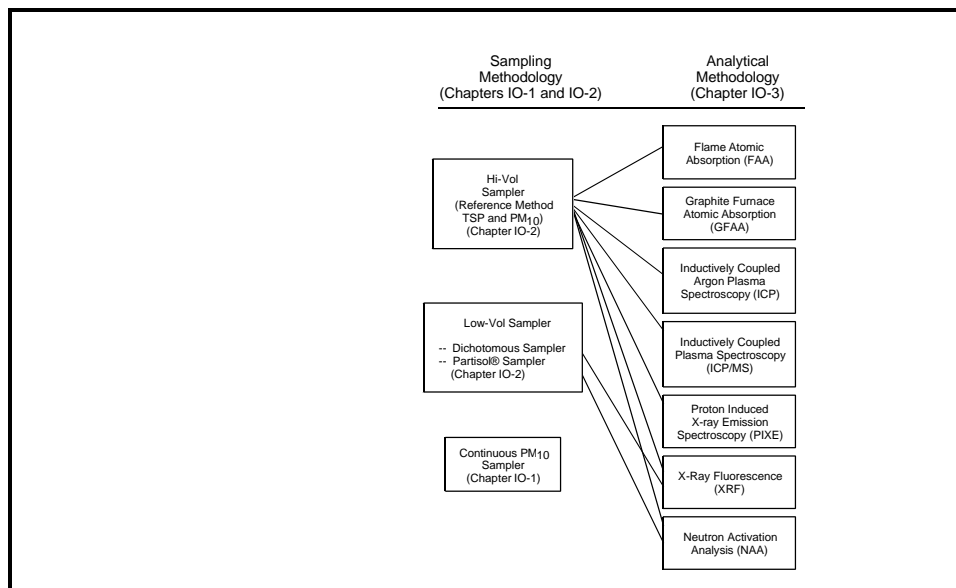

Figure 4-11. Compendium of inorganic methods for sampling and analysis of HAPs at HTRW sites

Table 4-12
Brief Method Description and Applicability for Organic and Inorganic Compendia

Organic Compendium		
Method No.	**Description**	**Types of compounds determined**
TO-1	Tenax GC adsorption and GC/MS analysis	Volatile, nonpolar organics (e.g., aromatic hydrocarbons, chlorinated hydrocarbons) having boiling points in the range of 80° to 200°C
TO-2	Carbon molecular sieve adsorption and GC/MS analysis	Highly volatile, nonpolar organics (e.g., vinyl chloride, vinylidene chloride, benzene, toluene) having boiling points in the range of -15° to +120°C
TO-3	Cryogenic trapping and GC/FID or ECD analysis	Volatile, nonpolar organics having boiling points in the range of -10° to +200°C
TO-4A	High volume PUF sampling and GC/MS analysis	Organochlorine pesticides
TO-5	Dinitrophenylhydrazine liquid impinger sampling and HPL/UV analysis	Aldehydes and ketones
TO-6	High performance liquid chromatography (HPLC)	Phosgene
TO-7	Thermosorb/N adsorption	N-nitrosodimethylamine
TO-8	Sodium hydroxide liquid impinger with high performance liquid chromatography	Cresol/phenol
TO-9A	High volume PUF sampling with high resolution gas chromato-graphy/high resolution mass spectrometry (HRGC/HRMS)	Polyhalogenated Dioxin/Furans
TO-10	Low volume polyurethane foam (PUF) sampling with gas chromatography/ electron capture detector (GC/ECD)	Pesticides
TO-11A	Adsorbent cartridge followed by high performance liquid chromatography (HPLC) detection	Formaldehyde
TO-12	Cryogenic preconcentration and direct flame ionization detection (FID)	Non-methane organic compounds (NMOC)
TO-13A	PUF or PUF/XAD-2 adsorption with GC/MS detection	Polynuclear aromatic hydrocarbons (PAHs)
TO-14A	SUMMA® passivated canister sampling with GC/MS detection	Non-polar volatile organic compounds
TO-15	SUMMA® passivated canister sampling with GC coupled to a MS or ion trap	Polar and nonpolar volatile organic compounds
TO-16	Real-time monitoring by fourier transform infrared spectroscopy (FTIR)	Volatile organic compounds
TO-17	Real-time or solid adsorbent sampling followed by GC/MS (or alternate) detection	Volatile organic compounds

Table 4-12 (continued)

|	Inorganic Compendium	
Method No.	**Description**	**Types of compounds determined**
Chapter 1		
IO-1.1	Graseby PM_{10} Beta Attenuation	SPM at the 10μ cut size
IO-1.2	Thermo PM_{10} Beta Attenuation	SPM at the 10μ cut size
IO-1.3	R&P PM_{10} TEOM® Sampler	SPM at the 10μ cut size
Chapter 2		
IO-2.1	High-volume sampler	Total SPM
IO-2.2	Dichotomous sampler	SPM at the 10μ and 2.5μ cut size
IO-2.3	R&P Partisol® sampler	SPM at the 10μ cut size
IO-2.4	Air volume calculation	Calculate standard air volume
Chapter 3		
IO-3.1	Filter selection, preparation, and extraction	Filter management
IO-3.2	Analysis of filter by atomic absorption (AA)	Analysis for metals
IO-3.3	Analysis of filter by X-ray fluorescence (XRF)	Analysis for metals
IO-3.4	Analysis of filter by Inductively Coupled Plasma (ICP) spectroscopy	Analysis for metals
IO-3.5	Analysis of filter by ICP/MS	Analysis for metals
IO-3.6	Analysis of filter by Protein Induced X-Ray emission Spectroscopy (PIXE)	Analysis for metals
IO-3.7	Analysis of filter by Neutron Activation Analysis (NAA)	Analysis for metals
Chapter 4		
IO-4.1	Measurement of atmospheric strong acidity using annular denuder	Analysis for SPM pH
IO-4.2	Measurement of atmospheric reactive gases and fine particles using annular denuder	Analysis for sulfates, nitrates, PM_{10}, pH, etc.
Chapter 5		
IO-5.1	Measurement of atmospheric mercury concentration	Analysis for mercury
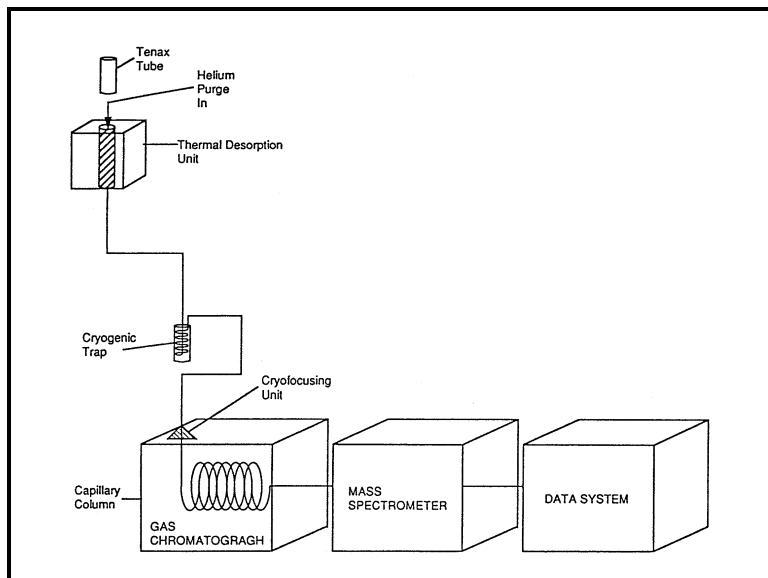
Figure 4-12. Compendium Method TO-1 Analytical Scheme

pass through the cartridge. The cartridge is then transferred to the laboratory and analyzed. For analysis, the cartridge is placed in a heated chamber and purged with an inert gas. The inert gas transfers the VOCs from the cartridge onto a cold trap and subsequently onto the front of the GC column, which is held at low temperature (e.g., -70°C).

Method TO-1 has numerous interferences including Tenax® contamination, compound breakthrough during collection on Tenax®, and artifact formation on the adsorbent during sampling. The analysis procedure also involves a "one-chance" analysis and leaves no reanalysis options when method QC failures.

(b) *Organic Compendium Method TO-2: Volatile Organic Compounds (-15° to +120°C).* Compendium Method TO-2 is similar to Method TO-1 except the adsorbent is a carbon molecular sieve (CMS) rather than Tenax®. This sieve allows some of the more volatile organics, i.e., vinyl chloride, to be captured and analyzed.

Method TO-2, which may also be replaced with TO-17, is suitable for the determination of certain nonpolar VOCs having boiling points in the range of -15° to 120°C. The analytical detection limit varies with the analyte. Detection limits of 0.01 to 1 ppbv are achievable using a 20-liter sample.

Sampling involves drawing ambient air through a cartridge containing ~0.4 g of a CMS adsorbent. Volatile organic compounds are captured on the adsorbent while major inorganic atmospheric constituents pass through (or are only partially retained). Prior to the actual laboratory analysis the cartridge is purged with 2 to 3 liters of pure, dry air (in the same direction as sample flow) to remove adsorbed moisture.

Similar to Compendium Method TO-1, the cartridge is heated to 350° to 400°C, under helium purge, and the desorbed organic compounds are collected in a specially designed cryogenic trap. The collected organics are then flash evaporated onto a capillary column GC/MS system (held at -70°C). The individual components are identified and quantified during a temperature programmed chromatographic run, as illustrated in Figure 4-12.

Similar to Method TO-1, contamination of the CMS, sampling compound breakthrough, and artifact formation are potential weaknesses of the TO-2 methodology and also is limited to a single analysis.

(c) *Organic Compendium Method TO-3: Volatile Organic Compounds (-10° to 200°C).* Compendium Method TO-3 involves the collection of VOCs having boiling points in the range of -10° to 200°C in a
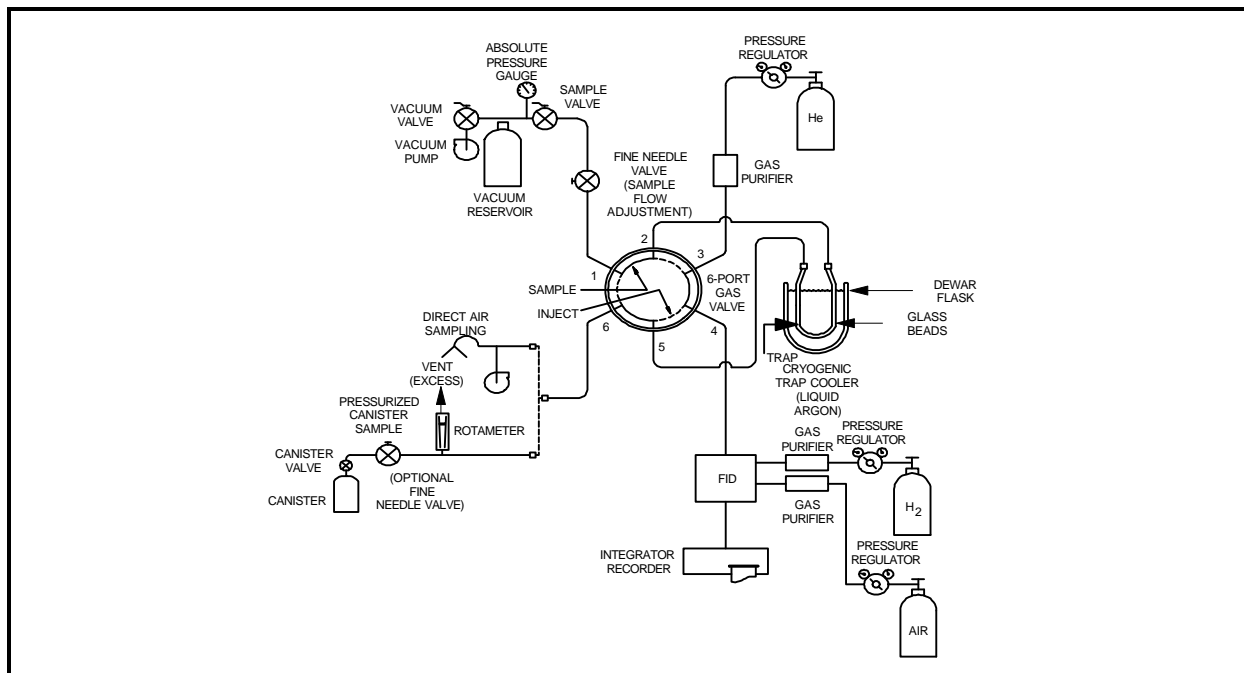
Figure 4-13. Compendium Method TO-3 Sampling and Analytical Methodology

cryogenic trap constructed of copper tubing packed with glass beads, as illustrated in Figure 4-13. The collection trap is submerged in either liquid oxygen or argon. Liquid argon is highly recommended because of the safety hazard associated with liquid oxygen. With the sampling valve in the fill position, an air sample is admitted into the trap by a volume measuring apparatus. In the meantime, a GC column oven is cooled to a subambient temperature (-50°C) for sample analysis. Once sample collection is completed, the value is switched so that the carrier gas sweeps the contents of the trap onto the head of the cooled GC column. Simultaneously, the liquid cryogen is removed, and the trap is heated to assist the sample transfer process. The GC column is temperature programmed, and the component peaks eluting from the columns are identified and quantified using flame ionization and/or electron capture detection. Alternate detectors (e.g., photoionization) can be used as appropriate. An automated system incorporating these various operations as well as the data processing function has been described in the literature. Due to the complexity of ambient air samples, high resolution (capillary column) GC techniques are recommended. However, when highly selective detectors (such as the electron capture detector) are employed, packed column technology without cryogenic temperature programming can be effectively used in some cases.

(d) *Organic Compendium Method TO-9A: Dioxins/Furans*. Compendium Method TO-9A is used for the determination of polyhalogenated dibenzo-p-dioxins and dibenzofurans (PHDDs/PHDFs) in ambient air. This includes polychlorinated dibenzo-p-dioxins and dibenzofurans (PCDDs/PCDFs), and bromo/chloro dibenzo-p-dioxins and bromo/ chloro dibenzofurans (BCDDs/BCDFs).

As illustrated in Figure 4-14, ambient air is drawn at a flow rate about 200 to 280 L/min into a high volume sampler, which includes a quartz fiber filter and cleaned and quality assured polyurethane foam (PUF) backup adsorbent cartridge. Figure 4-15 depicts a typical TO-9A adsorbent cartridge. Sampling is normally performed for 24-hours. During sampling, the dioxin/furans are retained on the adsorbent cartridge. After sampling, the filter and PUF are placed in an ice chest and shipped to the laboratory at ambient temperatures where they are analyzed for specific analytes using high resolution GC/high resolution MS (HRGC/HRMS).

The sampling system consists of a vacuum pump capable of drawing an airflow of about 200 to 280 L/min, a dual sampling module, a flow venturi, an elapsed time indicator, a 7-day timer, and an anodized aluminum shelter.

Prior to analysis, the filter and PUF are combined and spiked with surrogate compounds and Soxhlet extracted with benzene or toluene for 16 hours. The resulting extract is then subjected to an acid/base cleanup procedure followed by cleanup procedures on micro columns of silica gel, alumina, and carbon. The extract is spiked again to determine method efficiencies achieved from previous spikes and then concentrated for HRGC/HRMS analysis.
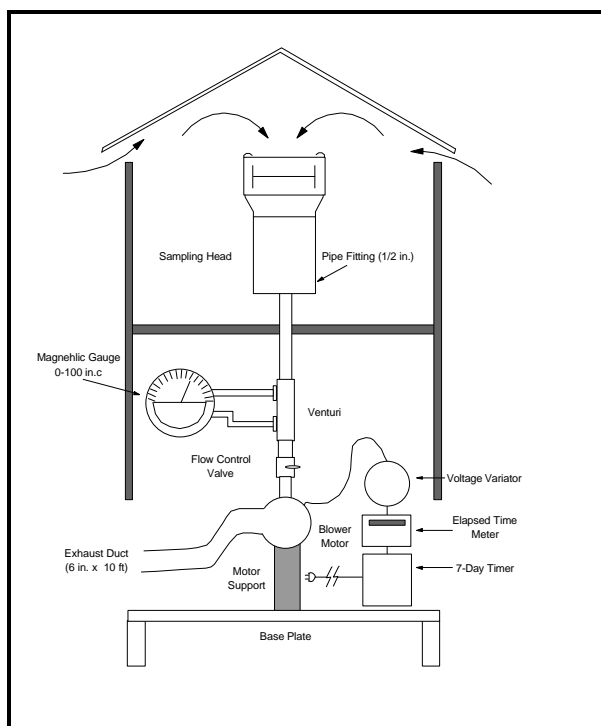

Figure 4-14. Compendium Method TO-9A Sampler for Dioxins/Furans
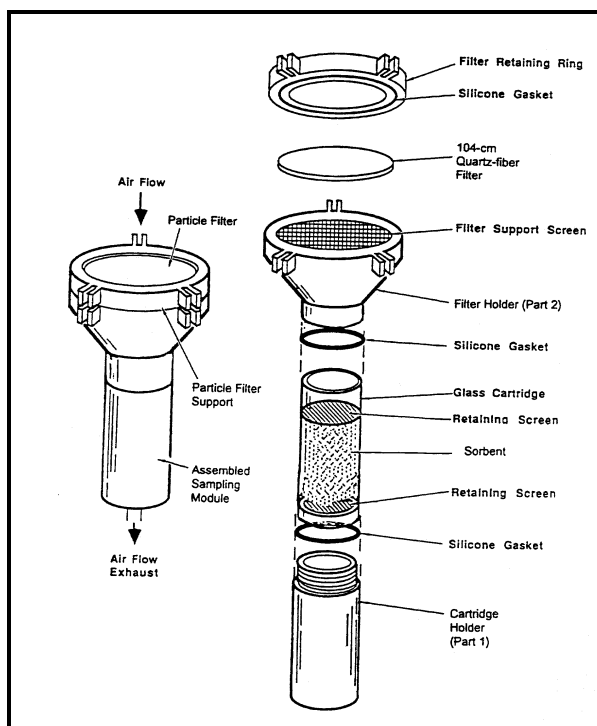

Figure 4-15. Example of TO-9A adsorbent cartridge used for capturing dioxins/furans

Analysis is performed using HRGC/HRMS operated in the select ion monitoring (SIM) mode using a 30-m SE54 or 60-m SP-2231 fused silica capillary column. This analysis determines the sampler efficiency, method efficiency, and the concentrations achieved for the PHDDs/PHDFs. The analytical results and volume of air sampled are used to calculate the concentrations of other compounds.

The major components of the analytical system are the HRGC/HRMS with data system and the Soxhlet extraction system. The HRGC should be equipped for temperature programming, and the injection port should be designed for capillary columns. The HRMS system should be operated in the electron impact ionization mode, and the static resolving power of the instrument should be maintained at 10,000 (10 percent valley definition). The system should be operated in the SIM mode with a total cycle time of 1 second or less. The same set of ions should be used for both calibration and sample analysis. The HRGC/HRMS must be equipped with a data system to provide for instrument control and data acquisition, processing, and storage.

(e) *Organic Compendium Method TO-12: Nonmethane Organic Compounds (NMOC).* As discussed earlier, regulatory agencies have required perimeter air monitoring programs at HTRW sites to monitor NMOC as a first level indicator of emission with subsequent analysis for speciated VOCs if the NMOC value at the perimeter exceeds a predetermined threshold value. Compendium Method TO-12 is a technique for monitoring NMOC either on a real-time basis or by utilizing time-integrated technique. This method involves a simple cryogenic preconcentration procedure with subsequent direct FID sample analysis, similar to Compendium Method TO-3. The method is sensitive and provides accurate measurements of ambient NMOC concentrations where speciated data are not required.

Method TO-3 involves the collection of VOCs in a trap cooled to -160°C and analyzed by GC/FID for compound speciation, while Method TO-12 combines the same type of cryogenic concentration technique but using a simple GC/FID for a total NMOC determination, without the GC columns and complex procedures necessary to achieve species separation (as illustrated in Figure 4-13).

Compendium Method TO-12 can be used either for direct, in situ ambient measurements or (more commonly) for analysis of integrated samples collected in specially treated stainless steel or silanized canisters. The use of sample canisters allows for the collection of integrated air samples over an extended time period by unattended, automated samplers providing a TWA sample result.

In the integrated mode, an ambient air sample is extracted into a pre-evacuated treated stainless steel canister, either through the utility of a metal bellows pump, as illustrated in Figure 4-16 or by using the initial vacuum as a means of sample extraction.
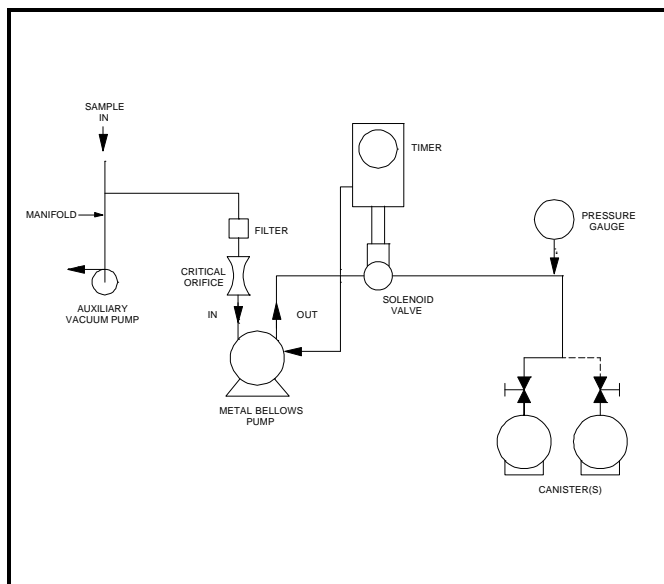
Figure 4-16. Compendium Method TO-14A sampling system using pressurized treated stainless steel canister(s)

In the in situ mode, a whole air sample is extracted directly from the ambient air and delivered to the analytical system for analysis on-site.

As illustrated in Figure 4-13, the analysis requires drawing a fixed-volume portion of the sample air, either from the canister or in situ, at a low flow rate through a glass-bead filled trap that is cooled to approximately -186°C with liquid argon.

The cryogenic trap simultaneously collects and concentrates the NMOC (either via condensation or adsorption) while allowing the methane, oxygen, etc., to pass through the trap without retention. The system is dynamically calibrated so that the volume of sample passing through the trap does not have to be quantitatively measured, but must be precisely repeatable between the calibration and the analytical phases. After the fixed-volume air sample has been drawn through the trap, a helium carrier gas flow is diverted to pass through the trap, in the opposite direction to the sample flow, and into an FID. When the residual air and methane have been flushed from the trap and the FID baseline restabilized, the cryogen is removed and the temperature of the trap is raised to approximately 90°C.

The NMOC compounds previously collected in the trap revolatilize due to the increase in temperature and are carried into the FID, resulting in a response peak or peaks from the FID. The area of the peak or peaks is integrated, and the integrated value is translated to concentration units via a previously-obtained calibration curve relating integrated peak areas with known concentrations of propane.

By convention, concentrations of NMOC are reported in units of parts per million carbon (ppmC), which, for a specific compound, is the concentration in units of part per million by volume (ppm$_v$) multiplied by the number of carbon atoms in the compound.

(f) *Organic Compendium Method TO-13A: Semi-Volatiles*. Organic Compendium Method TO-13A is used for the determination of benzo(a)pyrene [B(a)P] and other PAHs in ambient air. The 16 compounds which have been quantitatively analyzed by GC/FID and GC/MS using this method are:

Acenaphthene	Benzo(e)pyrene
Acenaphthylene	Benzo(g,h,i)perylene
Anthracene	Benzo(k)fluoranthene
Benz(a)anthracene	
Benzo(a)pyrene	

Chrysene
Dibenz(a,h)anthracene
Fluoranthene
Fluorene
Indeno(1,2,3-cd)pyrene
Naphthalene
Phenanthrene
Pyrene

In operation, ambient air is drawn at a flow rate of about 200 to 280 L/min into a high-volume sampler equipped with a quartz fiber filter and backup PUF or organic resin adsorbent cartridge (see Figure 4-15).

The sampling system (see Figure 4-14) is similar to Compendium Method TO-9A and consists of a vacuum pump capable of drawing an airflow of about 200 to 280 L/minute, dual sampling module, flow venturi, elapsed time indicator, 7-day skip timer, and an anodized aluminum shelter. The semivolatiles in the ambient air are retained on the filter or backup adsorbent cartridge.

The sampling period is about 4 to 24 hours, depending on the expected ambient pollutant concentration. After sampling, the samples are stored in an ice chest at 20°C until receipt at the analytical laboratory, at which time they are stored refrigerated at 4°C. The filter and cartridge are analyzed for PAHs using GC/MS, GC/FID, or high performance liquid chromatography (HPLC) with UV (to determine naphthalene, acenaphthylene, and acenaphthene) or fluorescence detectors (to determine the remaining PAHs). Sample holding time should not exceed 20 days.

The choice of PUF or XAD-2 resin as the filter backup adsorber depends on the target compounds of interest. XAD-2 is reported to have a higher collection efficiency for the more volatile PAHs (naphthalene, acenaphthylene, and acenaphthene) than PUF as well as a higher retention efficiency for both volatile and reactive PAHs. On the other hand, PUF adsorbers are easier to handle in the field and have been successfully used for collecting organochlorine pesticides and PCBs.

Some limitations of the method are that the collection efficiency from other compounds not listed in the method or identified elsewhere in the literature must be determined by the user. In addition, problems with baseline noise, baseline drift, peak resolution, and changes in sensitivity may occur in HPLC analysis. Also, heat, ozone, NO_2, and UV light may cause sample degradation. These problems should be addressed in the user prepared project specific SOP.

(g) *Organic Compendium Method TO-14A: Volatile Organic Compounds (-15° to 170°C).* Organic Compendium Method TO-14A is used for the determination of VOCs in ambient air at HTRW sites.

Ambient air samples are collected using treated passivated stainless steel or silanized canisters; VOCs are subsequently separated by GC and measured by mass-selective detector or multidetector techniques. The 40 organic compounds that have been successfully collected in pressurized canisters by this method are:

Freon 12 (Dichlorodifluoromethane)   Methyl chloride (Chloromethane)

Freon 114 (1,2-Dichloro-1,1,2,2-tetrafluoroethane)
Vinyl chloride (Chloroethylene)
Methyl bromide (Bromomethane)
Ethyl chloride (Chloroethane)
Freon 11 (Trichlorofluoromethane)
Vinylidene chloride (1,1,-Dichloroethene)
Dichloromethane (Methylene chloride)
Freon 113 (1,1,2-Trichloro-1,2,2-trifluoroethane)
1,1-Dichloroethane (Ethylidene chloride)
cis-1,2-Dichloroethylene
Chloroform (Trichloromethane)
1,2-Dichloroethane (Ethylene dichloride)
Methyl chloroform (1,1,1-Trichloroethane)
Benzene (Cyclohexatriene)
Carbon tetrachloride (Tetrachloromethane)
1,2-Dichloropropane (Propylene dichloride)
Trichloroethylene (Trichloroethene)
cis-1,3-Dichloropropene (cis-1,3-dichloropropylene)
1,1,2-Trichloroethane (Vinyl trichloride)

Toluene (Methyl benzene)
trans-1,3-Dichlorpropene (trans-1,3-Dichloro propylene)
1,2-Dibromomethane (Ethylene dibromide)
Tetrachloroethylene (Perchloroethylene)
Chlorobenzene (Phenyl chloride)
Ethylbenzene
m-Xylene (1,3-Dimethylbenzene)
p-Xylene (1,4-Dimethylxylene)
Styrene (Vinyl benzene)
1,1,2,2-Tetrachloroethane
o-Xylene (1,2-Dimethylbenzene)
1,3,5-Trimethylbenzene (Mesitylene)
1,2,4-Trimethylbenzene (Pseudocumene)
m-Dichlorobenzene (1,3-Dichlorobenzene)
Benzyl chloride (α-Chlorotoluene)
o-Dichlorobenzene (1,2-dichlorobenzene)
p-Dichlorobenzene (1,4-dichlorobenzene)
Hexachlorobutadiene (1,1,2,3,4,4-Hexachloro-1,3- butadiene)

Compendium Method TO-14A represents two sampling procedures, depending on the type of sample collected: sub-atmospheric pressure sampling and pressurized canister sampling. Subatmospheric pressure sampling is used to take grab samples (duration 10 to 30 seconds) or time-integrated sample (duration 12 to 24 hours). The integrated samples are taken through a flow-restrictive inlet (i.e., mass flow controller) as illustrated in Figure 4-16. The canister is evaluated to 0.05 mm Hg; when opened to the atmosphere, the differential pressure causes the sample to flow into the canister. Pressurized sampling is used when longer-term integrated samples or higher volume samples are required. A pump and flow control device is used to achieve a final canister pressure of 103 to 206 kPa (15 to 30 psig). A metal bellows-type pump draws in air from the sampling manifold to fill and pressure the canister.

Subatmospheric pressure and pressurized canister sampling systems are commercially available and have been used as part of EPA's Toxic Air Monitoring Stations (TAMS), Urban Air Toxic Pollutant program (UATP), and the non-methane organic compound (NMOC) sampling and analysis program.

After the air sample is collected, the canister valve is closed, an identification tag is attached to the canister, and the canister is transported to a predetermined laboratory for analysis. Upon receipt at the laboratory, the canister tag data is recorded and the canister is attached to the analytical system. During analysis, water vapor is reduced in the gas stream by a Nafion® dryer (if applicable), and the VOCs are then concentrated by collection in a cryogenically-cooled trap, as illustrated in Figure 4-17.

The cryogen is then removed and the temperature of the trap is raised. The VOCs originally collected in the trap are revolatilized, separated on a GC column, then detected by one or more detectors for identification and

quantitation. The analytical strategy for Method TO-14A involves using a high-resolution GC coupled to one or more appropriate GC detectors As described in Paragraph 4.3, GC detectors can be divided into two groups: specific and nonspecific detectors. The nonspecific detectors include, but are not limited to, the NPD, the FID, the ECD, and the PID. The specific detectors include the MS operating in either the SIM mode or the SCAN mode, or the ion trap detector.

(h) *Organic Compendium Method TO-15: Volatile Organic Compounds (-75° to 120°C)*. Compendium Method TO-15 is distinguished from the TO-14A method in that it (1) addresses a more extensive set of compounds (the VOCs mentioned in Title III of the CAAA of 1990, which includes many VOCs that cannot be addressed by the TO-14 method), (2) uses GC/MS techniques as the only means to identify and quantitate target compounds; (3) establishes method performance criteria for acceptance of data, allowing the use of alternate but equivalent methods; and (4) includes variations in canister construction materials.

Compendium Method TO-15 sampling is identical to Method TO-14A. After sampling, the canister is returned to the laboratory for analysis. Compendium Method TO-15 uses the dry purge of solid adsorbents as a water management technique; a known volume of sample is directed from the canister and through a concentration trap. Prior to analysis, co-collected water vapor is reduced by dry purging the concentration trap without the loss of target compounds. After the drying and concentration steps are completed, the VOCs are thermally desorbed, entrained in a carrier gas stream, and carried onto a GC column for separation. As an alternative to the dry purge
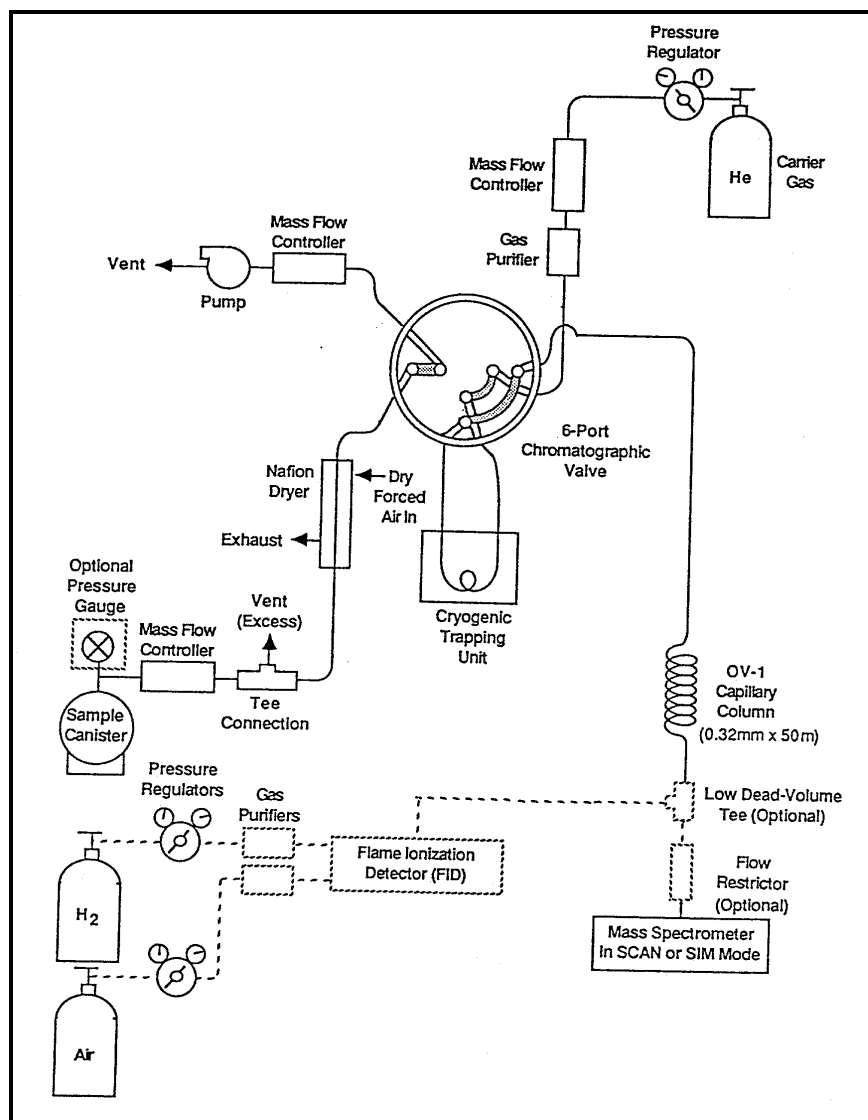
Figure 4-17. Compendium Method TO-14A analytical scheme

water management technique, the amount of water vapor in the sample can be reduced below any threshold for affecting the proper operation of the system by reducing the sample size. For example, a small sample can be concentrated on a cold trap and released directly to the GC column. The reduction in sample volume may require an enhancement of detector sensitivity. Other water management approaches are also acceptable as long as the approaches do not eliminate compounds on the target list.

The analytical strategy for Method TO-15 involves using a high resolution GC coupled to a mass spectrometer. If the mass spectrometer is a linear quadruple system, it is operated either by continuously scanning a wide range of mass to charge ratios (SCAN mode) or by monitoring selected ions indicative of a target list of compounds (SIM mode). If the mass spectrometer is based on a standard ion trap design, only a scanning mode is possible. Mass spectra for individual peaks in the total ion chromatogram are examined with respect to the fragmentation pattern corresponding to various VOCs and including the intensity of primary and secondary ions. The fragmentation pattern is compared with stored spectra taken under similar conditions to identify the compound. For any given compound, the intensity of the primary fragment is compared with the system response to the primary fragment for known amounts of the compound to establish the compound concentration that exists in the sample.

(i) *Organic Compendium Method TO-16: Volatile Organic Compounds (-15° to 170°C).* Compendium Method TO-16 involves the use of FTIR for monitoring emissions from an HTRW sites. In operation, an IR source is set at one end of the site with a receiver at the other end of the site. The sample is the source emissions or ambient atmosphere along a line-of-sight between the source and detector. The current pathlength is limited to about 1,000 m but can be extended to 3 km with the addition of an auxiliary telescope. This design is the most useful mode of operation for fenceline monitoring and area source emission verification. There are several obvious advantages to using optical monitoring over conventional point sampling. They are:

- Spectra stored for later identification.

- Use as a survey screening tool.

- Real-time assessment of temporal and spacial profile of volatile organics from the site.

- Reasonable cost per analyte.

- Usability with a tracer release for dispersion modeling.

Optical sensing is effective for measuring a variety of inorganic gases and volatile organic gases that have absorption features in the infrared or ultra-violet spectrum.

The basic components of an extractive FTIR system include a transmitter, receiver, and electronic system. In operation, IR light projected across an open area and returned using a retro reflector to the optical detection system. The heart of the optical detection system is the Michelson-type interferometer.

(j) *Organic Compendium Method TO-17: Volatile Organic Compounds (-25° to 170°C).* Compendium Method TO-17 is similar to Compendium Method TO-1 and TO-2 but allows for use of adsorbents other than Tenax®. Method TO-17 describes a procedure for the sampling and analysis of VOCs in ambient air at sub-ppb, ppb and ppm levels. The method is based on pumping a volume of air through a sorbent tube to collect and concentrate VOC pollutants. The VOCs are subsequently analyzed using a fully automated thermal desorption-capillary GC procedure:

- Stage 1: Sample transferred to preconcentrator step.

- Stage 2: Dry purge sorbent tube with ~200 mL pure inert gas before analysis, if required.

- Stage 3: Thermal desorption of the sorbent tube (primary desorption).

- Stage 4: Separation by high resolution capillary GC.

- Stage 5: Measurement by MS or conventional GC detectors.

The method is applicable to all vapor-phase organic air pollutants that meet the following criteria:

• Volatility range n-C3 to n-C20.

• Compatible with standard GC analysis.

(2) *EPA Inorganic Compendium.*

(a) *Inorganic Compendium Chapter IO-1: Continuous Measurement of PM$_{10}$ in Ambient Air.* Inorganic Compendium Chapter IO-1 contains EPA equivalent instrumental methods for PM$_{10}$ that give a continuous measurement of ambient PM$_{10}$ concentration. The method addresses two different measurement principles that have received EPA's approval as equivalent methods: the beta attenuation monitor (BAM) uses beta radiation, and the tapering element oscillating microbalance (TEOM$^®$) uses an oscillating pendulum as the measurement technology. Those methods that compose Chapter IO-1 of the Inorganic Compendium are:

• Inorganic Compendium Method IO-1.1: Continuous Monitoring of Ambient PM$_{10}$ Concentration Using the Graseby PM$_{10}$ Beta Attenuation Monitor.

• Inorganic Compendium Method IO-1.2: Determination of PM$_{10}$ in Ambient Air Using the Thermo Beta Gauge Automated Particle Sampler.

• Inorganic Compendium Method IO-1.3: Determination of PM$_{10}$ in Ambient Air Using the R&P Continuous TEOM$^®$ Particulate Sampler.

Unlike the reference methods, the equivalent methods allow concentration to be tracked in near real-time. This feature is useful when parameters such as the diurnal variation in concentration or the change in concentration associated with certain activities on the HTRW site are of interest.

Compendium Method IO-1.1 utilizes the Graseby beta gauge monitor, which directly measures particulate mass at concentrations of 0.005 to 20 milligrams per cubic meter (mg/m^3) on a real-time basis using the beta attenuation technique. This instrument provides half-hourly and daily averages and affords the potential for limited subsequent chemical analysis of the particulate samples. With certain specifications, the Andersen instrument has been designated as an equivalent method for determining 24-hour average PM$_{10}$ concentration in ambient air by the EPA under Designation No. EQPM-0990-076, effective September 18, 1990. The monitor described in detail in Method IO-1.1 presents the configuration and operation of the instrument as an equivalent method for PM$_{10}$.

The Graseby beta instrument operates by drawing ambient air through a PM$_{10}$ inlet head at a flow rate volume of 16.7 liters per minute. The air containing PM$_{10}$ enters the instrument where it is pulled through the glass fiber filter tape, and the particles are deposited on the tape. Low level beta radiation is emitted from a stainless steel capsule, containing Krypton-85 gas, towards the filter tape containing deposited PM$_{10}$. The particle matter on the tape reduces the intensity of the beta radiation reaching the measuring chamber on the opposite side of the tape. To compensate for the effect of the filter tape on the reduction of the level of beta radiation, the source directs a second beam of beta particles through a "foil" that mimics clean filter tape to a second measuring chamber (compensation chamber). No airflow is directed to the compensation foil so the effect of the foil on the beta radiation intensity remains constant. The instrument compares the measurement of the

compensation foil to the measurement of the filter tape with deposited PM_{10} to determine the mass of the particulate matter. Because changes in temperatures, pressure, or humidity can affect PM_{10} measurement of the filter tape, the measurements made through the compensation foil are impacted to the same degree. The foil measurements provide baseline data to compensate for these meteorological effects. This monitor is less sensitive to temperature, pressure, and humidity fluctuations than some other types of continuous particle monitors because of the compensation foil measurements that provide baseline data. Because the measuring mechanism lacks moving parts, the instrument is not as sensitive to vibrational effects as other types of continuous particulate monitors.

The Graseby monitor has certain limitations or interferences. In high-humidity or rainy climates, water may collect on the filter tape and cause artificially high mass readings. In these same climates, where the instrument is housed in an air-conditioned environment, the ambient air inlet tube should be insulated to avoid condensation or the inlet tube heater used to ensure that any water drawn into the unit is vaporized. For the specific beta particle source used in this instrument, any replacement or maintenance work on the source may only be performed by trained personnel with radiological authorization.

Compendium Method IO-1.2 uses the Thermo beta gauge monitor, which operates under the same basic principles as the Graseby monitor, but with some differences. This instrument was designated as an equivalent method for PM_{10} by the EPA under Designation No. EQPM-0391-081, effective March 5, 1991. The Thermo monitor can measure ambient mass concentration with a resolution of about 3 micrograms per cubic meter ($\mu g/m^3$) for a 1-hour sampling period. A constant volumetric flow rate for the PM_{10} inlet of 18.9 L/min is used compared to the 16.67 L/min for the Graseby unit. A major difference between the two monitors is the beta source. The Thermo monitor uses a carbon-14 beta source compared to Krypton-85 gas for the other monitor. The carbon-14 source does not require a license by the Nuclear Regulatory Commission, whereas the Krypton-85 does.

Different from the β-gauges, the Inorganic Compendium Method IO-1.3 uses the Rupprecht and Pataschnick (R&P) Continuous PM_{10} Monitor, which is based upon a tapering element oscillating microbalance (TEOM®) as a filter-based measurement system to continuously measure particulate mass at concentrations between 5 $\mu g/m^3$ and several grams per cubic meter (g/m^3) on a real-time mass monitoring basis. The instrument calculates mass rate, mass concentration, and total mass accumulation on exchangeable filter cartridges that are designed to allow for future chemical and physical analysis. In addition, this instrument provides for hourly and daily averages. This system operates on the principal that particles are continuously collected on a filter cartridge mounted on the tip of a tapered hollow glass element. The element oscillates in an applied electric field. With this monitor, particle-laden air enters through an air inlet and then passes to the sensor unit containing the patented microbalance system. The inlet system may or may not be equipped with an optional sampling head to preseparate particles at either a 2.5 or 10 μm diameter. The R&P PM_{10} inlet is designed to allow only particulate matter ≤ 10 μm in diameter to remain suspended in the sample air stream as long as the flow rate of the system is maintained at 16.67 L/min. The monitor can be operated as a TSP monitor or as a PM_{10} monitor.

In operation, the sample stream passes into the microbalance system, which consists of a filter cartridge and oscillating hollow tube, where the stream is heated to a predetermined temperature. The filter cartridge is a half-inch diameter thin aluminum base (foil-like) assembly. A water resistant plastic cone, which fits onto the

oscillating element, is attached to the aluminum base. An automatic flow controller pulls the sample stream through the monitor at flow rates between 0.5 and 5 L/min. The wider end of the hollow element is fixed to a platform and is vibrated at its natural frequency. The oscillation frequency of glass element is maintained based on the feedback signal from an optical sensor.

As mass accumulates on the filter cartridge, the resonant frequency of the element decreases, resulting in a direct measurement of inertial mass. Based upon the direct relationship between mass and frequency, the monitor's microcomputer calculates the total mass accumulation on the filter, and the mass rate and mass concentration in real-time.

The TEOM® monitor is very sensitive to mass concentration changes and can provide precise measurements for sampling durations of 1 hour or less. To achieve this level of precision, the hollow glass element must be maintained at a constant temperature to minimize the effects of thermal variations. Because the instrument's primary operating mechanism is the microbalance system, the instrument should be isolated from mechanical noise and vibrations as much as possible. The operating temperature of the element can be lowered to minimize the potential particle loss bias for more volatile compounds but must be maintained above the maximum ambient temperature encountered during the field sampling.

(b) *Inorganic Compendium Chapter IO-2: Time-Integrated Measurements of Suspended Particulate Matter (SPM) in Ambient Air.* Inorganic Compendium Chapter IO-2 contains both reference and equivalent time-intergrated methods for monitoring total SPM, PM_{10} and $PM_{2.5}$ concentration. These methods that compose Chapter IO-2 are:

- Method IO-2.1: Sampling of Ambient Air for Suspended Particulate Matter (SPM) Using High Volume (HV) Sampler.

- Method IO-2.2: Sampling for Suspended Particulate Matter in Ambient Air Using a Dichotomous Sampler.

- Method IO-2.3: Sampling of Ambient Air for Suspended Particulate Matter Using Low Volume Partisol® Sampler.

Inorganic Compendium Method IO-2.1, Suspended Particulate Matter (SPM) Monitoring Using High Volume (HV) Sampler, is the EPA reference method for TSP and is codified at 40 CFR 50, Appendix B. This method uses a high-volume sampler (hi-vol) to collect particles with aerodynamic diameters of approximately 100 μm or less. The hi-vol samples 40 to 60 ft^3/min of air with the sampling rate held constant over the sampling period. The hi-vol's design causes the TSP to be deposited uniformly across the surface of the filter. The TSP hi-vol can be used to determine the average ambient TSP concentration over the sampling period, and the collected material can subsequently be analyzed to determine the identity and quantity of inorganic metals present in the TSP.

Modifications to the inlet of the sampler used in Compendium Method IO-2.1 allows the measurement of PM_{10}. The PM_{10} hi-vol is identical to the TSP hi-vol except that it is equipped with an inlet that directs only PM_{10} particulate matter to the filter.

The Federal reference method for PM_{10} measurements is based on particulate selection by inertial separation followed by filtration and gravimetric determination of the PM_{10} mass on the filter substrate. The referenced method for PM_{10} is codified at 40 CFR 50, Appendix J. The standard for this method specifies the features for a reference PM_{10} measurement method. These features are summarized as follows:

- The sampling inlet has a cut-point of 10 $\pm$0.5 μm aerodynamic diameter, as determined in a wind tunnel using liquid particles of specified diameter at specific wind speeds.

- Flow-rate remains stable over a 24-hour period, independent of filter loading, within $\pm$5 percent of the initial average flow reading and within $\pm$10 percent of the initial flow rate for instantaneous flow measurements.

- Measurement precision for a 24-hour period should be within $\pm$5 μg/m^3 for concentrations less than 80 μg/m^3 or $\pm$7 μg/m^3 of measured PM_{10} for concentrations greater than 80 μg/m^3.

- For a nominal air volume sampled over a 24-hour period, the filter media should collect more than 99 percent of a 0.3 μm particles and have an alkalinity of <25 microequivalents per gram and a net equivalent weight gain or loss of not more than 5 μg/m^3.
- Prior to weighing, the filter should be equilibrated at constant temperature ($\pm$3 percent) between 15° and 30°C and constant relative humidity ($\pm$5 percent) between 20 and 45 percent.

Inorganic Compendium Method IO-2.2, Dichotomous Sampler for Monitoring PM_{10} and $PM_{2.5}$, is a method for determining of inhalable particles with diameters of less than 10 micrometers.

A dichotomous sampler is used to separate the particles by size, into coarse particles (2.5-10 μm) and fine particles (less than 2.5 μm). A ring-mounted 37-millimeter Teflon® filter is used to collect particles.

In operation, the particles enter the sampler inlet at a flow rate of 17.6 L/min where they are separated into fine (less than 2.5 μm) and coarse (2.5-10 μm) fractions by a virtual impactor. Constant air flow through the system is maintained by a mass flow controller. The sampling duration usually varies from 12 to 24 hours depending upon experimental design and amount of ambient air particulate present. The particles are collected on 37 mm diameter Teflon® filters. Filters are analyzed for specific trace metals by X-ray fluorescence (XRF) spectrometry.

Inorganic Compendium Method IO-2.3, Partisol Samplers, is a microprocessor-controlled manual sampler with a unique set of features that make it a suitable platform for the measurement of particulate concentration, acid aerosol, and other constituents found in the atmosphere. When equipped with a PM_{10} inlet and operated in its most basic mode, the hardware performs the same function as traditional high-volume PM_{10} samplers. For some apportionment or traffic studies, the device can be set up to sample by wind velocity and/or direction, or by time of day.

In operation, ambient air is drawn through a low flow (16.7 L/min) PM_{10} or $PM_{2.5}$ inlet where particle size selection takes place. The particulate-laden air is then directed through a collection filter composed of either quartz, Teflon®-coated glass, or Teflon®, where the particulate matter is collected. A mass flow control system maintains the sample flow through the system at the prescribed volumetric flow using information from sensors

that measure the ambient temperature ($^{\circ}$C) and ambient pressure (atmospheres). A piston pump provides the vacuum necessary to draw the sample stream through the inlet, filter, and mass flow controller. A microelectronics system provides the user with menu-driven programming and diagnostic and data storage capabilities.

The sample filter is conditioned and weighed both before and after sample collection to determine the amount of mass collected during the sampling period, which is 24 hours for EPA reporting purposes. As is the case with all filter-based manual samplers, proper filter handling is an important element in the computation of valid mass concentration results.

As a general rule, a PM_{10} sampler is used, except for the following two cases, at HTRW sites: (1) when deposition (particularly for larger particles) is of concern because of the potential for ingestion through contact with surfaces (i.e., lead ingestion); or (2) when toxic compounds (usually metals) may be present in the larger size particles. Usually this occurs when the source of the particulate matter is from grinding or erosion of soil or ore. If more detailed information on both inhalation and ingestion as routes of exposure is required, both TSP and PM_{10} sampling may be needed.
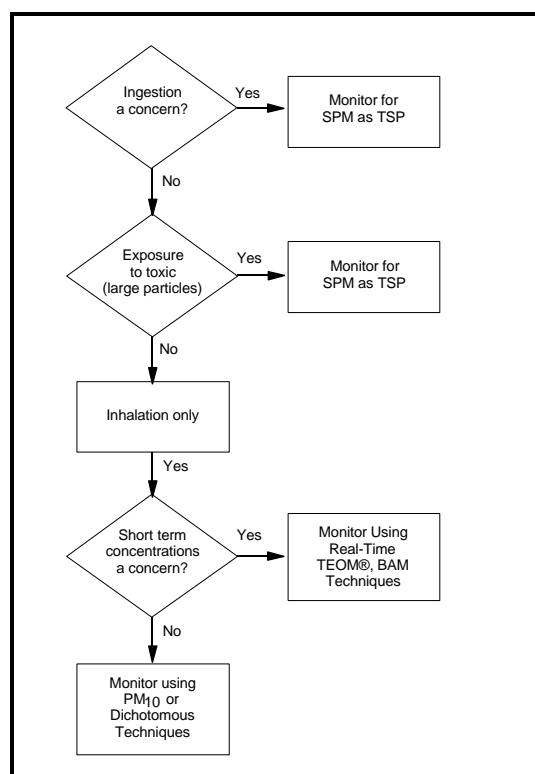

Figure 4-18. Example of a PM$_{10}$ Sampling Decision Tree for HTRW sites.

In deciding between integrated (PM_{10} and dichotomous) and near real-time samplers (BAM and TEOM$^{®}$) for PM_{10}, the following points should be considered. Generally, integrated sampling is preferred for the compounds of concern. Near real-time samplers are used if short-term variations in SPM are of interest. The information from the BAM and TEOM$^{®}$ would be used to estimate short-term concentration levels of certain SPM constituents with certain assumptions about time variation in composition of SPM. At this point, analysis of samples from BAM and TEOM$^{®}$ is experimental and needs to be further developed.

If only SPM is of interest, the PM_{10} hi-vol sampler with size selective inlet and quartz fiber filter is generally used because it allows for the collection of a large volume of air sample. However, analysis for some particulate compounds may not be as sensitive on quartz fiber filters. In that case, the dichotomous sampler would be used. Separation of fine particles from coarse particles is also possible with the dichotomous sampler, making it preferable when doing a more refined risk assessment.

In deciding between the BAM and TEOM$^{®}$ sampler, factors such as cost, need for a climate-controlled shelter, etc., must be considered. Figure 4-18 presents a PM_{10} sampling decision tree, which can be used for HTRW sites involving

the perimeter air monitoring program. Table 4-13 discusses the advantages/disadvantages associated with sampling methods discussed above.

(c) *Inorganic Compendium Chapter IO-2.3: Chemical Species Analysis of SPM on Filters.* Inorganic Compendium Method IO-2.3 includes five options for quantitative analysis of particles collected on filter materials as discussed in Inorganic Compendium Chapters IO-1 and IO-2. They are:

- Atomatic absorption (AA) spectroscopy (Compendium Method IO-3.2).

- XRF spectroscopy (Compendium Method IO-3.3).

- Inductively coupled plasma (ICP) atomic emission spectroscopy (Compendium Method IO-3.4).

- Inductively coupled plasma/mass spectroscopy (ICP/MS) (Compendium Method IO-3.5).

- Proton induced X-ray emission (PIXE) spectroscopy (Compendium Method IO-3.6).

- Neutron activation analysis (NAA) (Compendium Method IO-3.4).

Several factors influence the selection of an analysis option. These include cost, the elements for which the analytical method can be used, the number of samples and number of elements to be determined per sample, and sensitivity for the elements of interest. Table 4-14 illustrates the comparison of the analytical techniques with their associated weaknesses and strengths.

In XRF analysis, the sample is irradiated with one or more X-ray beams, and the elements in the sample emit X-rays at characteristic wavelengths. The wavelengths detected indicate which elements are present, and the quantity of each element is determined from the intensity of the X-rays at each characteristic wavelength. XRF analysis can be used for all elements with atomic weights from 11 (sodium) to 92 (uranium), and multiple elements can be determined simultaneously. This analysis technique is nondestructive and requires minimal sample preparation--the filter is inserted directly into the instrument for analysis. This technology is relatively inexpensive, but the detection limit is higher than other analysis techniques. Typically, analytical costs are about $100 per sample. Analysis by XRF typically involves the collection of PM by dichotomous sampler, although a PM_{10} hi-vol sampler with quartz fiber filter or cellulose filter can also be used.

In ICP analysis, the sample is excited using an argon plasma "torch." When the excited atoms return to their normal state, each element emits a characteristic wavelength of light. The wavelengths detected and their intensity indicate how much of which elements are present. Up to 48 elements can be determined simultaneously. As with FAA and GFAA, the PM sample must be extracted and digested for ICP analysis, and the material introduced into the instrument is destroyed during analysis. An ICP instrument is more costly than FAA or GFAA instruments. The detection limit for GFAA is better than that for ICP for most elements. Analysis by ICP typically involves collection of PM by a hi-vol sampler.

Two atomic absorption (AA) analysis options are included in Inorganic Compendium Chapter IO-3: FAA and GFAA. The measurement principle is the same; the two options differ in how the sample is introduced into the instrument. Both types of atomic absorption spectroscopy involve irradiating the sample with light of a single wavelength and measuring how much of the input light is absorbed. Each element absorbs light at a characteristic wavelength; therefore, analysis for each element requires a different light source and only one element can be determined at a time. Analysis by AA typically involves collection of PM by a hi-vol sampler.

Table 4-13.
Advantages/Disadvantages Associated with Sampling Methods Presented in Inorganic Compendium Method IO-1

Sampling method	Advantages	Disadvantages
Hi-Vol Sampler (Reference Method)	•Collects TSP/PM$_{10}$ uniformly across the surface of filter •Can be used to determine average TSP/PM$_{10}$ concentration over the sampling period •Allows analysis of filter for metals •Because of higher flow rate, collects more material so lower ambient concentration of inorganic material can be detected •Simple to operate	•Requires 110V, 20-amp electrical service •Sampler is large and bulky and is not easily moved
Dichotomous Sampler (Reference Method)	•Capable of collecting size-fractionated PM •Operates at low flow rates, allowing for use of filter media which would clog quickly at high flow rates •Fairly low power requirements - could be adapted for remote use •Small, easy to handle	•Fairly complicated to operate •Small sample volume, which makes chemical analysis of collected PM difficult
BAM (Equivalent Method)	•Allows for real-time measurement of particulate concentrations (PM-10) •Reduces need for frequent filter changes because it uses a filter strip on which chemical analyses can be performed •Primary operating mechanism lacks moving parts, and is therefore not sensitive to vibrations that might adversely affect the accuracy of other continuous monitors •Less sensitive to temperature, pressure, and humidity fluctuations than other continuous monitors	•Cannot be used to differentiate or quantitate heavy metals and other PM of concern
TEOM® (Equivalent Method)	•Allows for real-time measurement of particulate concentrations	•Cannot be used to differentiate or quantitate heavy metals and other PM of concern •Sensitive to noise, temperature fluctuations

Table 4-14
Advantages/Disadvantages Associated with Analytical Options Discussed in Inorganic Compendium Chapter IO-3

	ADVANTAGE	DISADVANTAGE
FAA	• easy to use • extensive applications • low detection limits	• higher concentration • sample dissolution required • one (1) element at a time
GFAA	• well documented applications • lower detection limits than Flame AA	• limited working range sample • low sample throughput • one element at a time • more operator skill
ICP	• multi-element • high sample throughput • well documented applications • intermediate operator skill • linear range over 5 orders of magnitude	• more expensive (~120K) • sample dissolution is required • other elements can interfere
ICP / MS	• multi-elements • low concentrations • isotopic analysis • intermediate operator skills	• most expensive (~250K) • limited documented applications
PIXE	• multielement • non-destructive • minimal sample preparation	• standard/sample must match closely (matrix) • matrix offsets and background impurities may be a problem
XRF	• multielement • non-destructive • minimal sample preparation	• standard/sample must match closely (matrix) • matrix offsets and background impurities may be a problem
NAA	• multielement • non-destructive • minimal sample preparation • % to ppb range • high sample throughput • well documented applications	• some elemental interferences • standard sample matrix corrections • required access to research nuclear reactor

In FAA, the sample is atomized and introduced into the optical beam using a flame, typically air/acetylene or nitrous oxide/acetylene. In GFAA, a graphite furnace electrometer atomizer is used. These analytical techniques are destructive and require that the sample be extracted or digested in order to introduce it into the system in solution. GFAA instrumentation is the more expensive of the two. Typically, analytical costs are about $225 per sample. The detection limit for FAA is lower than for XRF; the detection limit for GFAA is typically about two orders of magnitude better than FAA.

Analysis by ICP/MS uses argon plasma torch to generate elemental ions for separation and identification by mass spectrometry. This analysis technique allows for greater than 60 elements to be determined simultaneously, and even the isotopes of elements can be determined. For ICP/MS analysis, the PM sample must be extracted or digested, and the analysis is destructive. ICP/MS analysis is the most expensive of those included in this method, but has the greatest sensitivity (lowest detection limit).

PIXE analysis is very similar to XRF analysis in that the sample is irradiated by a high energy source, in this case high energy protons, to remove inner shell electrons. Fluorescent X-ray photons are detected using the same detection methods as XRF. Analysis by PIXE also typically involves collecting SPM by dichotomous sampler.

Some of the analytical techniques listed above are typically used only with particular sampling methods. Figure 4-19 illustrates the relationships between sampling technologies and compatible analytical techniques. Furthermore, the type of filter medium used to capture the sample is a factor in the choice of analytical technique and vice-versa.
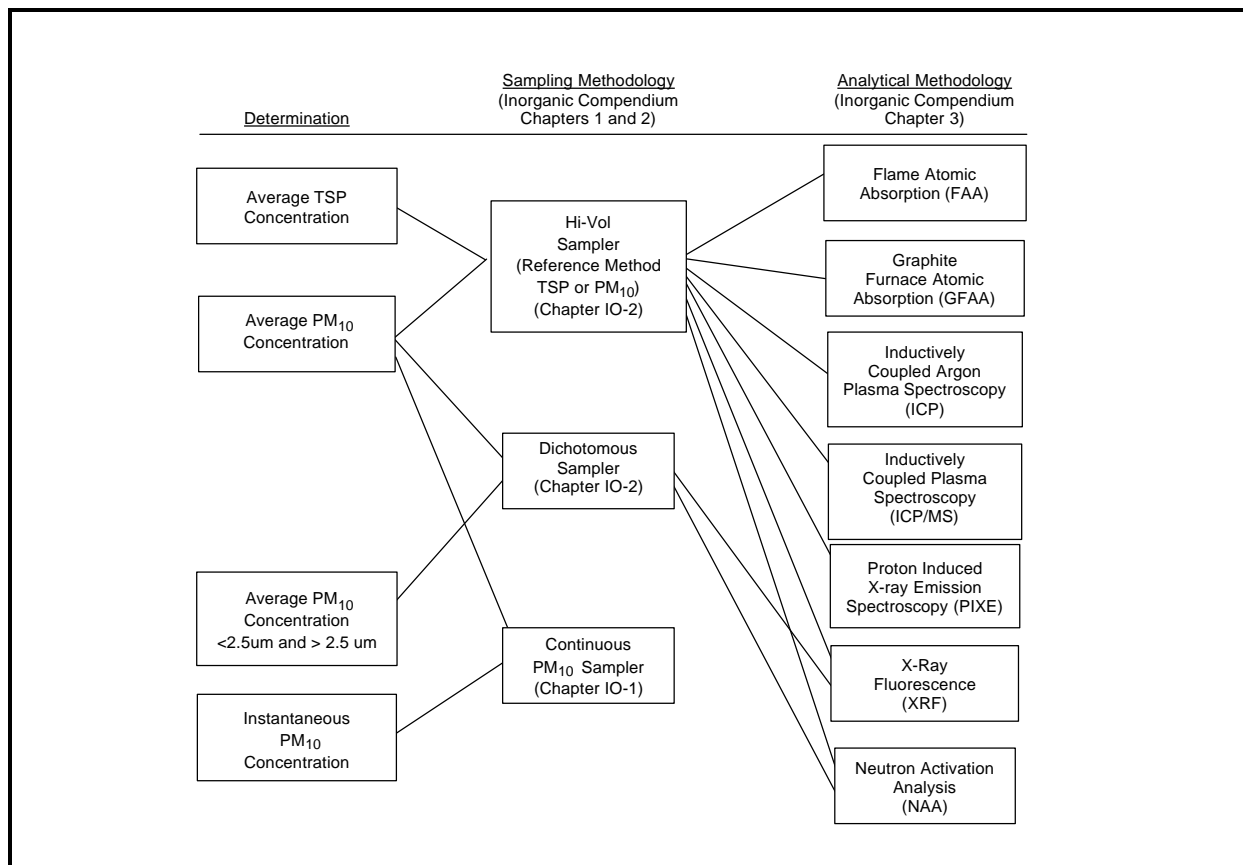
Figure 4-19. Relationship between sampling technologies and analytical techniques discussed in EPA's Inorganic Compendium.

Most importantly, the choice of analytical method will depend on the inorganic compounds of interest and the detection limits desired. Figure 4-20 provides a relative comparison of the ranges of detection limits that are typically for the various techniques. Table 4-15 provides a more detailed summary of the species measured and the respective minimum detection limits.

While factors such as element specificity and sensitivity are critically important, considerations such as cost and throughput (the number of samples and number of elements to be determined per sample) are also very important. Figure 4-21 provides a comparison of the various available analytical options discussed in Inorganic Compendium Method IO-3.

Figure 4-20 graphic content:

NEUTRON ACTIVATION ANALYSIS (NAA)					
ICP / MS					
GRAA					
ICP EMISSION					
PIXIE					
FLAME AA					
X-RAY FLUORESCENE					

0.01   0.1   1   10   100   1000

Detection limit, ng/m^3

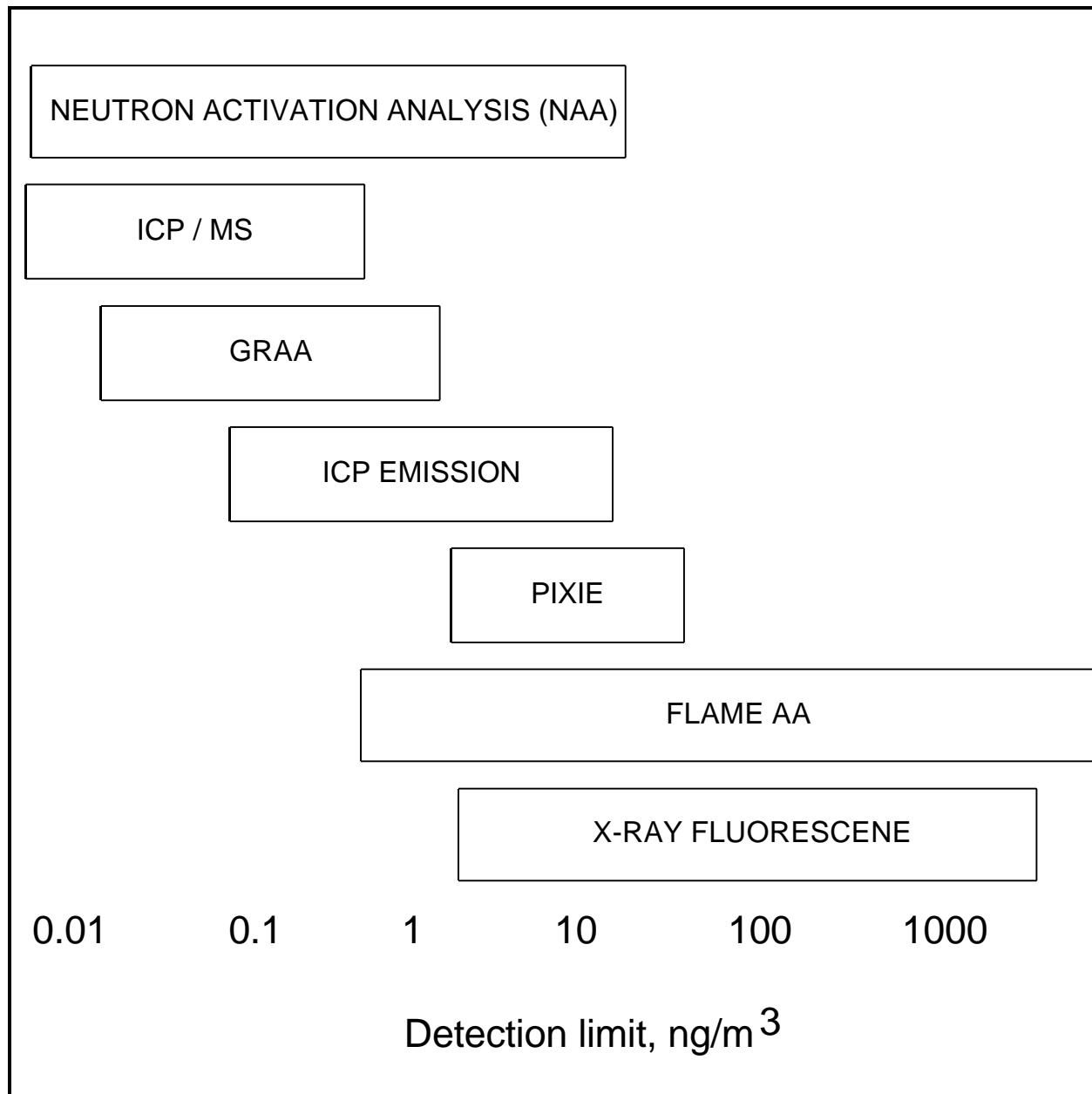**Figure 4-20. Typical detection limits for Inorganic Compendium Chapter IO-3 analytical options**

Table 4-15
Minimum Detection Limits (ng/m^3) of Ambient Air Samples For Different Inorganic Compendium Chapter IO-3 Analytical Methods[a]

Species	Analytical Technique						
	NAA	**XRF**	**PIXE**	**AAS**	**GFAA**	**ICP**	**ICP/MS**
Ag	0.12	6	NA	4	0.005	1	1.01
Al	24	5	12	30	0.01	20	1.01
As	0.2	0.8	1	100	0.2	50	1.10
Au	NA	2	NA	21	0.1	2.1	NA
Ba	6	25	NA	8	0.04	0.05	NA
Be	NA	NA	NA	2	0.05	0.06	0.02
Br	0.4	0.5	1	NA	NA	NA	NA
Ca	94	2	4	1	0.05	0.04	NA
Cd	4	6	NA	1	0.003	0.4	0.02
Ce	0.06	NA	NA	NA	NA	52	NA
Cl	5	5	8	NA	NA	NA	NA
Co	0.02	0.4	NA	6	0.02	1	0.01
Cr	0.2	1	2	2	0.01	2	0.01
Cs	0.03	NA	NA	NA	NA	NA	NA
Cu	30	0.5	1	4	0.02	0.3	0.01
Eu	0.006	NA	NA	21	NA	0.08	NA
Fe	4	0.7	3	4	0.02	0.5	0.01
Ga	0.5	0.9	1	52	NA	42	NA
Hf	0.01	NA	NA	2,000	NA	16	NA
Hg	NA	1	NA	500	21	26	NA
I	1	NA	NA	NA	NA	NA	NA
In	0.006	6	NA	31	NA	63	NA
K	24	3	5	2	0.02	NA	NA
La	0.05	30	NA	2,000	NA	10	NA
Mg	300	NA	20	0.3	0.004	0.02	0.02
Mn	0.12	0.8	2	1	0.01	0.1	0.02
Mo	NA	1	5	31	0.02	5	0.02
Na	2	NA	60	0.2	<0.05	NA	NA
Ni	NA	0.4	1	5	0.1	2	0.02
P	NA	3	8	100,000	40	50	NA
Pb	NA	1	3	10	0.05	10	0.01
Pd	NA	5	NA	10	NA	42	NA
Rb	6	0.5	2	NA	NA	NA	NA
S	6,000	2	8	NA	NA	10	NA
Sb	0.06	9	NA	31	0.2	31	0.01
Sc	0.001	NA	NA	50	NA	0.06	NA
Se	0.06	0.6	1	100	0.5	25	1.10
Si	NA	3	9	85	0.1	3	NA
Sm	0.01	NA	NA	2,000	NA	52	NA
Sn	NA	8	NA	31	0.2	21	0.01
Sr	18	0.5	2	4	0.2	0.03	NA
Ta	0.02	NA	NA	2,000	NA	26	NA
Th	0.01	NA	NA	NA	NA	63	NA
Ti	65	2	3	95	NA	0.3	0.01
Tl	NA	1	NA	21	0.1	42	0.01
U	NA	1	NA	25,000	NA	21	0.01
V	0.6	1	3	52	0.2	0.7	0.01
W	0.2	NA	NA	1,000	NA	31	0.01
Y	NA	0.6	NA	300	NA	0.1	0.01
Zn	3	0.5	1	1	0.001	1	0.01
Zr	NA	0.8	3	1,000	NA	0.6	

Table 4-15 (continued)

Species	Analytical Technique						
	NAA	**XRF**	**PIXE**	**AAS**	**GFAA**	**ICP**	**ICP/MS**
Cl	NA	NA	NA	NA	NA	NA	NA
NH_4	NA	NA	NA	NA	NA	NA	NA
NO_3	NA	NA	NA	NA	NA	NA	NA
SO_4	NA	NA	NA	NA	NA	NA	NA
Elemental Carbon	NA	NA	NA	NA	NA	NA	
Organic Carbon	NA	NA	NA	NA	NA	NA	NA

[a] Minimum detection limit is three times the standard deviation of the blank for a filter of 1 mg/cm^2 areal density.

   ICP = Inductively Coupled Plasma Emission Spectroscopy.
   AAS = Flame Atomic Absorption Spectrophotometry.
  PIXE = Proton Induced X-ray Emissions.
   XRF = X-ray Fluorescence.
   NAA = Instrumental Neutron Activation Analysis.
  GFAA = Graphite Furnace Atomic Absorption Spectroplometry
ICP/MS = Inductively Coupled Plasma Emission/Mass Spectroscopy.

Unfortunately, no one analytical methods can address all data quality objectives for a particular ambient air monitoring program. Each method has its own attributes, specifies, advantages, and disadvantages, as previously discussed.   However, Inorganic Compendium Chapter IO-3 attempts to bring together into one chapter the various analytical option, in a step-by-step methodology, to facilitate accurate and reliable data for SPM and metal concentration in the ambient air.

4-5. System Alarm Configuration

Because personnel are not always available to review data as it is generated by an air monitoring network, a system alarm is necessary to alert on-site staff to periods when their oversight is necessary. Such an alarm system must monitor instrumentation to determine when emissions of targeted compounds exceed action levels or when system upsets occur that could prevent the monitoring system from detecting upsets. The alarm system must then be capable of alerting on-site staff of these conditions. The following paragraphs discuss some specific considerations pertinent to the design of an alarm system. These considerations include the components of an alarm system, conditions that should be considered as triggers, and suggested methods of notification.

There are three components to an air monitoring alarm system. They are the air monitoring instrument, a trigger circuit, and a notification system.
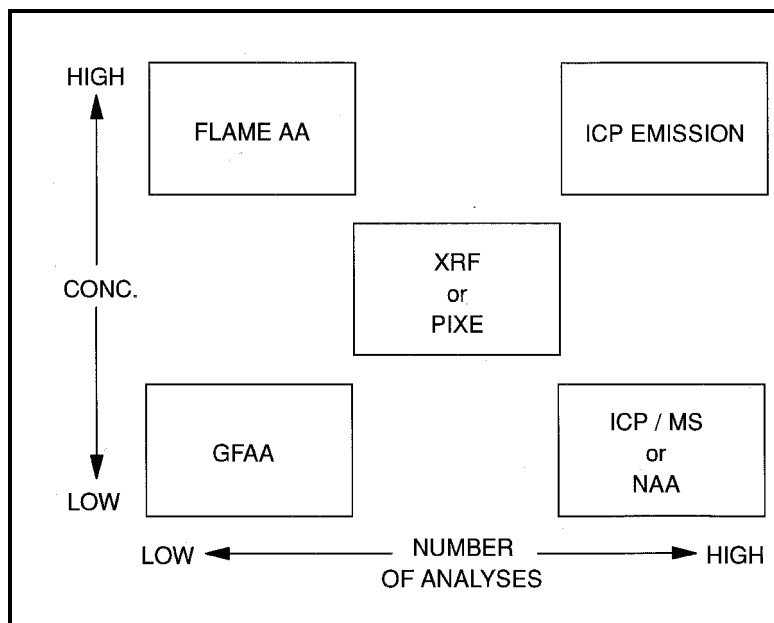
Most real-time air monitors have all three of these components integral to the instrument in the form of audible alarms. These alarms could be configured to alert personnel within the Analytical Center to excessive concentrations or instrument upsets. However, these alarms are typically not able to alert staff outside of the Analytical Center.

In the event that the selected air monitoring instrument is not equipped with an alarm feature, a computer with an analog to digital data card, a commercially available data logger, or a custom circuit can be used as a trigger for the alarm system.

A commercially available home security usually provides the most reliable and cost effective alert mechanism. These systems are available with time-proven smoke alarms, auto-dialers, weather-protected alarms, and backup power supplies. Other components are easily adapted as needed.

Figure 4-21. Throughput of analytical options in Chapter IO3

To be effective, the alarm system must be designed to monitor real-time air sampling instrumentation for exceedences of all project specific action levels. If backup monitors are available for use during failures of the primary real time monitoring system, these instruments must also be monitored by the alarm system. In addition, the alarm system should be designed to alert on-site staff to conditions that could adversely affect the operation of monitors or the alarm system itself. Some of these potential process upsets might include line voltage spikes or power outages, high wind speeds, or aberrations of critical instrumentation parameters (e.g., high or low over temperature, low flow rates, etc.).

The alarm system must be capable of notifying on-site staff, regardless of their location, whenever the air monitoring network is required to operate. If a staff member is always in the building or buildings in which the real-time air monitoring instrumentation is operating, then the alarm must be loud enough to be heard throughout the building, regardless of distracting activity. If a staff member will always be on the property but not necessarily in the same building(s) as the instrumentation monitors, during periods when the monitors are required to operate, an outdoor audible alarm system can be established in addition to the building alarm(s). If there will not always be a staff member on site during periods when the alarm system is required to operate, a remote notification system must be established. This system might include an

alarm to alert a guard, other on-site personnel, or a commercial security company by utilizing a auto-dialer to telephone or page air monitoring staff, or a frequency modulated (FM) transmitter.